PHOSPHORIC ACID, PHOSPHATES

AND

PHOSPHATIC FERTILIZERS

by

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GENERAL INTRODUCTION

American Chemical Society's Series of
Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities,

and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical sub-areas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.
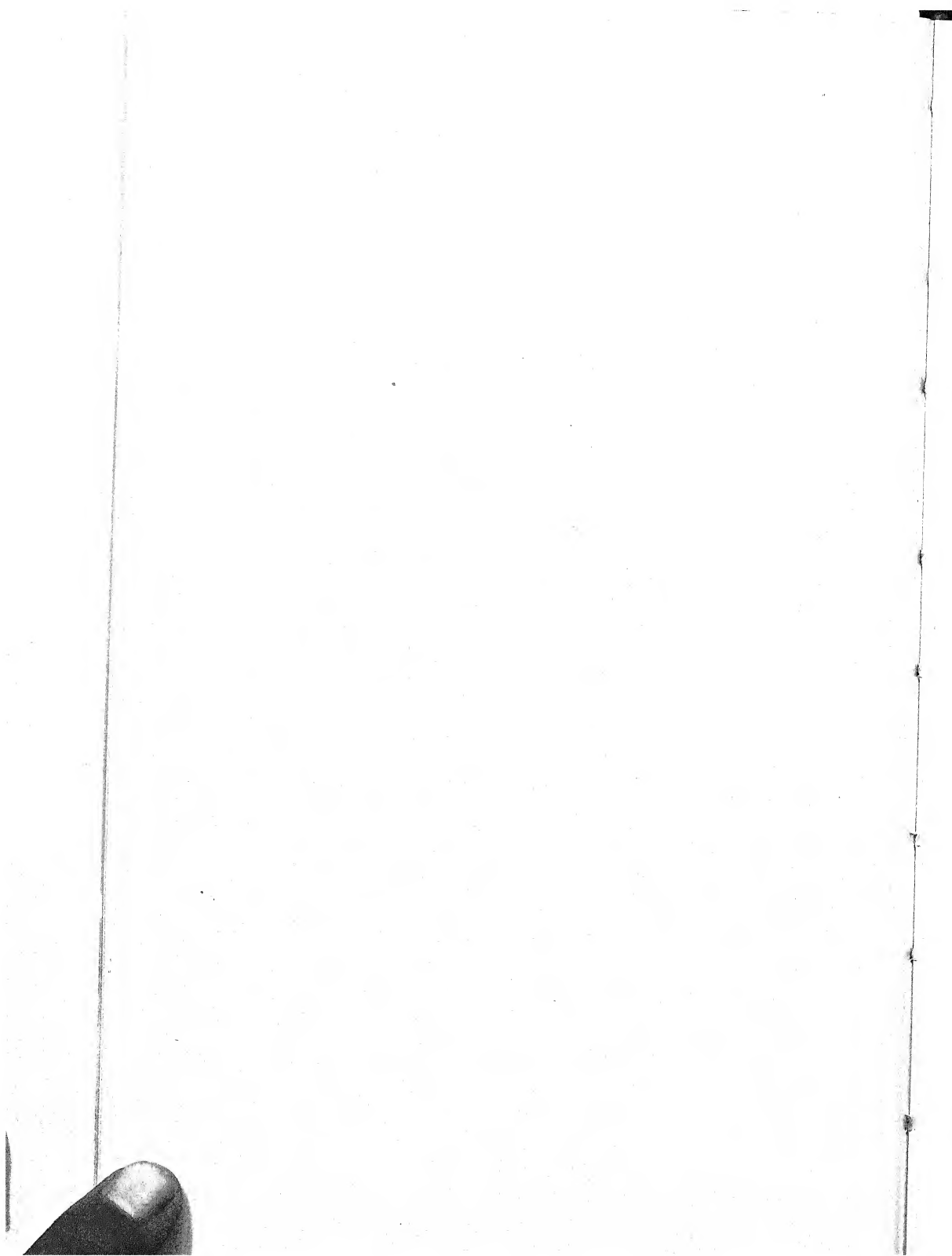
PREFACE

The great advances made in the manufacture of phosphorus, phosphoric acid and phosphate products since the first edition of this book was published in 1927 have made it necessary to expand and largely rewrite most of the chapters.

So many new and improved processes and products of phosphoric acid have been developed within and without the fertilizer industry that the writer felt it desirable to solicit the collaboration of competent authorities who were more familiar than he with certain phases of this broad subject. The author is deeply grateful to these collaborators whose names appear on the individual chapters prepared by them.

This book is designed to be a standard work of reference for those either engaged in, or contemplating the manufacture of phosphate products. It is hoped, however, that it will be useful not only to the highly trained technical man engaged in research and development, but also to plant superintendents and foremen responsible directly for the effective mining and recovery of phosphate rock and the manufacture therefrom of the numerous products that play such an important role in our national economy.
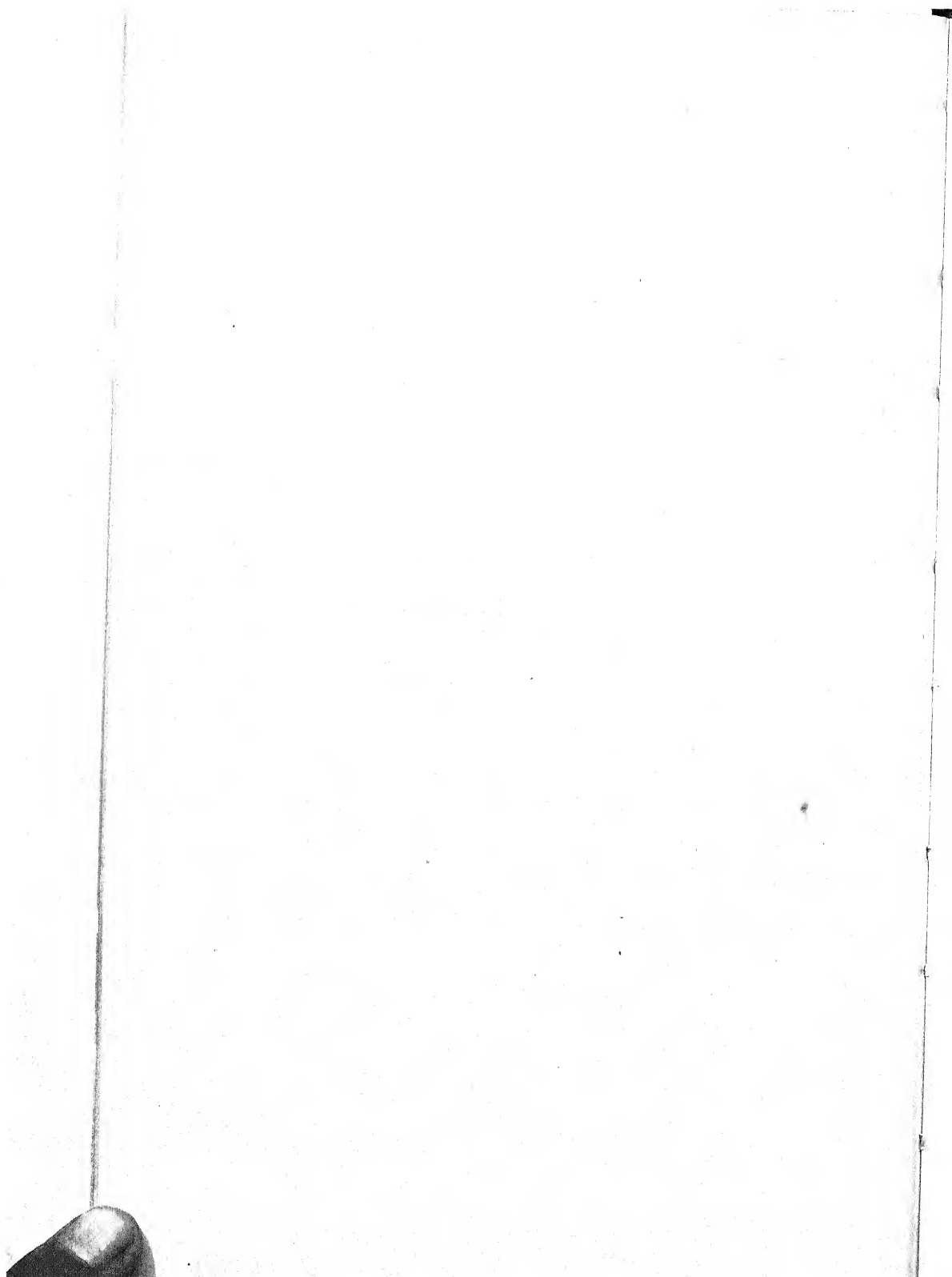
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1. Introduction

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Phosphoric acid has always played an essential part in many natural phenomena, particularly in the life of animals and plants. With the increase in the manufacture and use of artificial fertilizers it became a highly important commercial factor, and now that new improved methods have been developed for its more economic production, a much wider field is opening up for its industrial application. In fact it has in part displaced sulfuric acid for a number of purposes which require large tonnages of this universally used reagent.

Nearly all natural and industrial processes are dependent upon carbonic, sulfuric, nitric, hydrochloric and phosphoric acids and the several acids of silica. Either one or more of these relatively simple acids are essential constituents of the vast number of rocks and minerals which constitute the earth's crust. Through their chemical activity the alteration of minerals and the concentration of ore bodies are in part effected. Most of them play a major role in the cycle of life and death through the medium of which innumerable organic compounds are built up and again broken down. Finally the arts and industries as practiced by man, through which are evolved the manufactured products so essential to the maintenance and advance of civilization, could not be continued unless adequate supplies of these simple inorganic compounds were available.

Sulfuric acid and the acids of silica have so far proved to be the cheapest available for industrial use, and though they function under widely different conditions (the former being effective at relatively low temperatures and the latter only at high heat) they play more important roles in manufacturing processes than any of the other acids mentioned above.

The production of all modern structural materials, with the exception of gypsum, limestone and timber, whether they are of steel, copper, cement, clay or glass, is dependent upon the acids of silica. The manufacture of the bulk of our fertilizer materials and the refining and purification of innumerable finished products are brought about by sulfuric acid; in fact, all the other important inorganic acids have been or may be produced through the agency of sulfuric acid.

There is no possibility of any acid being substituted for the acids of

silica in most of their industrial applications since silica is either a constituent part of the products sought (such as cement, glass, tile, brick, etc.) or is present in the raw material (metalliferous ores) as an impurity which can only be removed by taking advantage of its acid properties.

The case of sulfuric acid, however, is quite different. The chemical activity of this reagent is frequently more important than the product of which it becomes a constituent part, and in many instances after the acid has been partly or wholly neutralized the sulfate radical of the salt or compound formed is relatively valueless or serves only as a carrier of a marketable ingredient. Now that other mineral acids (such as nitric and phosphoric) which form salts of high commercial value can be produced at a cost materially lower than was thought possible in the past, they can be substituted for sulfuric acid for a number of industrial purposes. The end products thus obtained are much enhanced in value.

Intense investigations on thermal methods of producing phosphoric acid, and the actual commercial development of these processes during the past 25 years, have given this acid a far more important role in the industries. It has actually displaced, for certain purposes, large tonnages of sulfuric acid, long considered the most economical reagent which could be employed.

Historical

The practice of using phosphatic materials as fertilizers goes back so far that there is no record of when and where they were first used. The dung of birds was used by the Carthaginians, over 200 years B.C., and cato and Columella[22], the earliest of agricultural writers, highly recommended the use of pigeon's dung for meadows, corn lands, and gardens. The use of bones, fish, and guano was also a very ancient practice. Although the last mentioned material was not introduced into Europe until 1839[24], it was used by the Incas of Peru[9], long before the Spaniards conquered that country and was so highly prized that it was a capital offense to kill the young birds on the guano islands. The effectiveness of dung was attributed by Palissy[18] in 1550 to the soluble salts which it contained.

While these three fertilizer materials were for many years the world's chief source of phosphoric acid, the nature of this compound was not discovered until long after the isolation and recognition of elemental phosphorus. This element was first prepared in 1669 by Brandt[13], an alchemist of Hamburg, Germany, in his search for the philosopher's stone. He evaporated large quantities of urine and obtained a substance luminous in the dark to which he named phosphorus.

Boyle[14] was the first to prepare phosphoric acid. In 1694, he reported that the action of water on the products of burning phosphorus yielded a liquid with acid properties. Shortly afterward, other investigators prepared this acid, but the determination of the elemental nature of phos-

phorus and the composition of phosphoric anhydride P_2O_5 are credited to Lavoisier[15].

Gahn[4], a Swedish chemist, apparently discovered that phosphorus is an essential constituent of the bones of men and animals (1769). Ten years later (1779) this same investigator found phosphorus in the mineral kinddom as lead phosphate (pyromorphite).

In 1775 Scheele[16] published a description of a method of producing phosphorus consisting in dissolving bones with nitric acid, precipitating out the lime with sulfuric acid, mixing the concentrated solution with charcoal, and heating the mass out of contact with air.

Guano and bones continued to be the main sources of phosphorus and phosphoric acid until after the middle of the nineteenth century. It is stated that the use of bones was so great in England during the early eighties that the battlefields on the Continent of Europe were turned by to supply Great Britain's demand for phosphates. In 1840 the Duke of Richmond[19] stated that the fertilizer value of bones was due not to the gelatin and fat but to the phosphoric acid which they contained; in the same year Liebig[21] suggested dissolving bones with sulfuric acid to render the phosphoric acid contained therein more soluble and available to crops. The treatment of bone ash with sulfuric acid is the subject of a British patent issued to John B. Lawes[10] in 1842.

This discovery marked the beginning of the immense superphosphate industry which is the basis of the fertilizer business in this country. Soon after this epoch-making practice was introduced, low grade mineral phosphates known as coprolites were developed in England[5]. Four to seven years later (1849–1852) low grade deposits of this mineral were recognized in several departments in France. The direct use of these mineral phosphates in a finely ground condition on the soil was advocated by Elie de Beaumont in 1856[5], but Liebig pointed out in 1857 that such phosphates could be dissolved with sulfuric acid just as readily as bone and thus rendered more efficient for agricultural purposes. This process was taken up so eagerly that five years later (1862) the annual production of superphosphates in England had reached 200,000 tons.

Phosphate baking powders were introduced into the United States at an early date, and a patent issued to E. N. Horsford[7] claims a substitute for tartaric acid in such products. The inventor called this substitute Pulverulent Phosphoric Acid, but his description of the method by which it was prepared shows it was actually impure monocalcium phosphate mixed with either flour or starch.

Forty years ago phosphoric acid in baking powders was derived almost entirely from bones, but with improvements in methods of purification and the commercial development of pyrolytic processes of producing this acid, phosphate rock became the main raw material used for this purpose.

Since 1867, when phosphate rock was first developed in South Carolina[25], the United States has been the foremost phosphate-producing nation in the world, not only supplying its own agricultural demands but a large proportion of the requirements of certain European and Asiatic countries.

In 1877 two Englishmen, Thomas and Gilchrist[23], developed a process in which phosphatic iron ores, up to that time considered of relatively little value, could be used in the production of steel low in phosphorus by causing this element to enter a highly basic slag. The phosphorus in this slag, while not in a water-soluble form, was found to be readily available to plants and quite effective in increasing crop yields. This discovery placed another large source of phosphoric acid at the disposal of the farmer, and several of the more progressive nations of Europe have been depending on basic slag to supply a substantial proportion of their agricultural demands for this fertilizer ingredient.

The effectiveness in the field of such slightly soluble materials as bones and basic slag led in the search for methods of determining the availability of these materials in the laboratory. As a result certain conventional test solutions have been established which are intended to approximate the solubility effect of the soil waters; the commercial values of phosphates are to a large extent based upon their complying with these tests. These regulations, coupled with the fact that a certain amount of prejudice exists toward fertilizers of an acid nature, have encouraged investigators to study other methods of treating phosphate rock besides that of rendering it soluble with the aid of sulfuric acid, but up to the present few have been commercially successful. A number of such typical schemes are discussed later and complete classified lists of these processes patented in the United States are given in the Tables of the Appendix.

ELEMENTAL PHOSPHORUS, OXIDES OF PHOSPHORUS AND THE ACIDS OF PHOSPHORUS

While this treatise deals chiefly with orthophosphoric acid and its compounds, the orthophosphates, certain derivatives of this acid are closely related thereto and play important roles in the laboratory, the factory, and in many industrial products. It is necessary, therefore, to devote some space to the occurrence, properties, and methods of preparing elemental phosphorus and its various other oxides and acids.

Phosphorus

This element, though widely distributed in nature, is never found in a free or uncombined state because of its great affinity for oxygen. With one or two minor exceptions[22], it exists in the mineral kingdom only in the form of phosphates, of which a large number have been identified.

As ordinarily prepared elemental phosphorus is a white or pale yellow

wax-like substance which becomes brownish yellow on exposure to light due to the formation of some red phosphorus. It has a specific gravity of 1.83, a melting point of 44.4°C and a boiling point of 287°C. It is insoluble in water but dissolves readily in carbon disulfide (18 to 1) from which it crystallizes in rhombic dodecahedra; it is also very soluble in the halogen compounds of phosphorus and slightly soluble in alcohol, ether, benzene, xylene, methyl iodide, glycerine, acetic acid and fused stearic acid. Phosphorus is luminous in the dark, possibly due to the formation of hydrogen phosphide (PH_3) which oxidizes in air. Other authorities explain phosphorescence on the basis that a preliminary oxidation of P to P_2O_3 takes place, the latter compound being oxidized further with simultaneous production of ozone and the surrounding air becoming ionized. This phenomenon of phosphorescence, however, is regarded by others as very complex. Even moist phosphorus oxidizes in air, evolving white fumes of phosphorous and phosphoric acids and phosphorus pentoxide. At slightly elevated temperatures, or when finely divided, it takes fire spontaneously in air, burning to phosphorus pentoxide. Molinari[20], however, states that it does not oxidize and may be distilled in pure dry oxygen. The element is a powerful reducing agent.

White or yellow phosphorus is very poisonous, 0.1 gram being sufficient to cause death. Post mortems have shown that the element is absorbed in the liver (which is distended) and in the blood. The chronic disease contracted by those who work in factories where yellow phosphorus is extensively used is known as necrosis of the bones, especially of the teeth and jaw. This disease was formerly quite prevalent among employees of match factories before the use of yellow phosphorus in matches was prohibited by law.

Phosphorus was first prepared in commercial quantities from bones and bone ash. Briefly, the method consisted in treating calcined or degelatinized bone with sulfuric acid, filtering or decanting off the solution of phosphoric acid or monocalcium phosphate from the gypsum, evaporating the solution to a specific gravity of 1.45, mixing it with 20 per cent of charcoal or coke, and again heating in shallow pans until the mass contained not over 6 per cent moisture. This mixture was then placed in terra cotta retorts, which were introduced into a suitable furnace and heated to redness for 24 hours, and then to a white heat for 48 hours. The phosphorus distilled off was collected under water and subsequently purified by redistilling.

This method of making phosphorus was cumbersome and costly and gave relatively low yields. It has been entirely supplanted by the electric furnace and blast furnace processes in which intimate mixtures of raw phosphate rock, silica and carbon (coke) are smelted directly under reducing conditions. Not only do these methods render the use of sulfuric acid unnecessary, but the processes are continuous and the yields obtained are much higher.

These thermal processes are now used successfully in the manufacture of phosphoric acid. They are discussed in detail in Chapter 10. Two allotropic forms of phosphorus are known, namely, black and red phosphorus. They are denser and have lower specific heats than the white variety. Black phosphorus is obtained by crystallization of the element from solution in molten metal, or by heating red phosphorus for a long period at 360°C in sealed tubes. This form of phosphorus is quite dense (specific gravity 2.69) and according to Mellor[17] is very stable. It has little or no commercial significance and some authorities doubt the existence of this allotropic form.

Red, or so-called amorphous phosphorus, discovered by Schrotter in 1845, and later found to really crystallize in the hexagonal system, is formed by exposing yellow phosphorus to light for a long period, or by prolonged heating at 250°C out of contact with air. This variety has a specific gravity of 2.3, a melting point (under pressure) of 725°C, is not phosphorescent, does not alter in air, is nonpoisonous and is not readily set on fire by friction; in fact it is not combustible until heated to a temperature of 200°C. Advantage is taken of the nonpoisonous character of red phosphorus in industry and it is now substituted for the yellow variety in a number of commercial operations.

Oxides of Phosphorus

There are four oxides of phosphorus, namely, phosphorus suboxide (P_4O), phosphorous oxide (P_4O_6), phosphorus tetroxide (P_2O_4) and phosphoric pentoxide (P_2O_5). Only two of these oxides, however, have much stability or importance commercially.

Phosphorus Suboxide (P_4O) has only been made as an interesting laboratory experiment. The usual method of preparation consists in dissolving yellow phosphorus in an alcoholic solution of potassium hydroxide. Hydrogen and phosphine are thus evolved and a bright red liquid remains which when acidified deposits a gelatinous mass composed mainly of P_4O. On filtering and repeatedly freezing, this oxide may be obtained in a relatively pure state as an orange-colored hygroscopic substance which readily burns to the higher oxides of phosphorus.

Phosphorus Oxide or Phosphorous Anhydride (P_4O_6) is obtained when yellow phosphorus is gently heated in a limited amount of dry air.

$$P_4 + 3O_2 \rightarrow P_4O_6$$
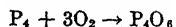
A certain amount of phosphoric anhydride (P_2O_5) is also formed at the same time but the former oxide, being more volatile than the latter, may be readily separated by sublimation.

Phosphorous oxide possesses a peculiar phosphorus-like odor. It forms

white crystals which run together into a wax-like mass melting at 22.5°C. It sublimes readily and boils out of contact with air at 173°C. Its vapor density shows its formula to be P_4O_6 and not P_2O_3 as formerly supposed and even now often expressed in writing chemical reactions involving its use. When dissolved in cold water phosphorous oxide forms a mixture of metaphosphorous acid (HPO_2) and phosphorous acid (H_3PO_3). With hot water it produces red phosphorus and orthophosphoric acid (H_3PO_4). Phosphorous oxide oxidizes very readily, catching fire in air and burning to P_2O_5.

Phosphorus Tetroxide (P_2O_4). By heating phosphorous oxide (P_4O_6) to 400°C phosphorus tetroxide (P_2O_4) and red phosphorus are produced.

$$4P_4O_6 \rightarrow 6P_2O_4 + P_4$$
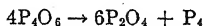
The tetroxide of phosphorus forms transparent crystals which react with water producing phosphorous and orthophosphoric acids. This oxide may be regarded as a mixture of phosphorous and phosphoric anhydrides just as nitrogen tetroxide (N_2O_4) is considered a mixture of nitrous and nitric oxides.

Phosphorus Pentoxide or Phosphoric Anhydride (P_2O_5) is the final product formed by the complete oxidation of phosphorus. It is the most important of the oxides of phosphorus and the most readily produced since all of the lower oxides tend to change over into this compound in the presence of air or other oxidizing media.

Phosphorus pentoxide is known in two modifications; the first is a crystalline product which sublimes at 250°C and when heated above this temperature is transformed into the second type, which is a soft white amorphous powder volatilizing only at red heat. Phosphoric anhydride is extremely hygroscopic so that it deliquesces in air and therefore must be stored and shipped in hermetically-sealed containers. Advantage is taken of its hygroscopic properties in the chemical laboratory where it is very useful as a desiccating agent.

Phosphoric anhydride dissolves in water with a hissing sound and evolution of heat, being converted successively and quickly into meta-, pyro-, and finally into orthophosphoric acid, the most important and useful of the oxyacids of phosphorus.

In stating the grade of various phosphatic materials used in the arts and industries the value is usually expressed in terms of P_2O_5 and hence this product is commonly though erroneously known as phosphoric acid.

The Acids of Phosphorus

There are eight known acids of phosphorus, five of which are formed by the combination of phosphorous and phosphoric anhydrides with definite

quantities of water, as shown in the following equations:

$$P_4O_6 + 2H_2O = 4HPO_2 = \text{Metaphosphorous acid} \qquad (1)$$
$$P_4O_6 + 6H_2O = 4H_3PO_3 = \text{Phosphorous acid} \qquad (2)$$
$$P_2O_5 + H_2O = 2HPO_3 = \text{Metaphosphoric acid} \qquad (3)$$
$$P_2O_5 + 2H_2O = H_4P_2O_7 = \text{Pyrophosphoric acid} \qquad (4)$$
$$P_2O_5 + 3H_2O = 2H_3PO_4 = \text{Orthophosphoric acid} \qquad (5)$$
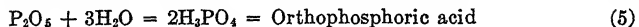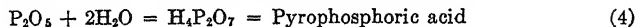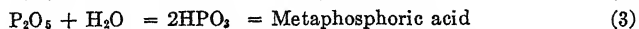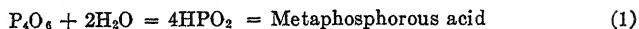
The other three acids of phosphorus, namely, hypophosphorous, pyro-phosphorous and hypophosphoric acid, are not ordinarily prepared by the interaction of water and the oxides of phosphorus.

Hypophosphorous Acid (H_3PO_2) or $O{:}P{-}\!\!\begin{smallmatrix}-OH\\-H\end{smallmatrix}$ is formed by heating a con-centrated solution of sodium hydroxide, lime, or barium hydroxide with white phosphorus. Phosphine and the alkali or alkaline earth hypophos-phite is formed according to the following equation:

$$4P_2 + 3Ba(OH)_2 + 6H_2O \rightarrow 3Ba(PO_2H_2)_2 + 2PH_3$$
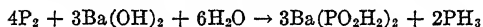
By treating the purified barium salt with sulfuric acid and filtering, free hypophosphorous acid is obtained, which can be concentrated under re-duced pressure to a syrupy consistency and even to the point where it crystallizes in white scales. At elevated temperatures hypophosphorous acid decomposes into phosphine and phosphoric acid. Hypophosphorous acid and the hypophosphites have a strong affinity for oxygen and hence are powerful reducing agents. Hypophosphorous acid reduces sulfuric acid to sulfur dioxide and the latter gas to elemental sulfur. It also separates such metals as gold, silver and mercury from certain of their salts, and thus has a distinct commercial value. The hypophosphites, even those of the heavy metals, are soluble in water but are not very stable, readily changing over to the more highly oxidized phosphites and phosphates.

Metaphosphorous Acid (HPO_2) or $O{:}P{-}OH$ is formed in slender crystals by the partial oxidation of phosphine under reduced pressure according to the following equation:

$$PH_3 + O_2 \rightarrow H_2 + HPO_2$$
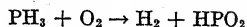
It is also obtained by the interaction of phosphorous anhydride and a limited amount of water as shown in Equation (1).

Like the other partially oxidized acids of phosphorus it is rather un-stable, going over to phosphorous and phosphoric acids on exposure to air or water. Metaphosphorous acid is of no commercial significance.

Pyrophosphorous Acid ($H_4P_2O_5$) or $\begin{smallmatrix}OH & & OH \\ \diagdown & & \diagup \\ P & \!\!-O-\!\! & P \\ \diagup & & \diagdown \\ OH & & OH\end{smallmatrix}$ is obtained
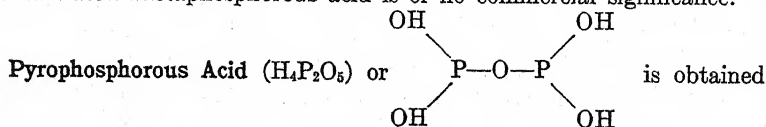
by continuously agitating a mixture of phosphorus trichloride (PCl_3) and phosphorous acid (H_3PO_3) for about 5 hours, keeping the mixture at a temperature of 30 to 40°C. This acid forms needle-like crystals which melt at 38°C and decompose in water to form phosphorous and phosphoric acids. Although pyrophosphorous acid and certain pyrophosphites have been made in the laboratory they have no industrial application.

Phosphorous Acid (H_3PO_3) or

$$OH \diagdown \diagup OH$$
$$P$$
$$|$$
$$OH$$

is formed along with phosphoric and hypophosphoric acids by the slow oxidation of phosphorus in moist air. It can be prepared more conveniently in the laboratory by adding phosphorus trichloride to water, taking care to keep the solution cool:

$$PCl_3 + 3H_2O \rightarrow + H_3PO_3 + 3HCl$$
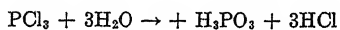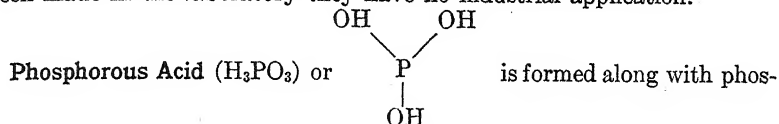
On evaporating this solution in vacuum, hydrochloric acid is evolved and a colorless crystalline hygroscopic mass of phosphorous acid is obtained which melts at 71°C, but is decomposed at higher temperatures into phosphoric acid and phosphine (PH_3).

The tendency of phosphorous acid to oxidize to phosphoric makes it a strong reducing agent though not as energetic in this regard as hypophosphorous acid. The salts of phosphorous acid (phosphites) differ from the hypophosphites in not being oxidized in air. Phosphorous acid is dibasic, forming two series of salts.

Hypophosphoric Acid ($H_4P_2O_6$) or

$$OH \diagdown \quad O \quad \diagup OH$$
$$P \qquad P$$
$$OH \diagup \quad O \quad \diagdown OH$$

may be considered a product formed by the extraction of water from one molecule of phosphoric acid and one molecule of phosphorous acid:

$$\left.\begin{array}{l} H_3PO_4 \\ \\ H_3PO_3 \end{array}\right\} - H_2O \rightarrow H_4P_2O_6$$
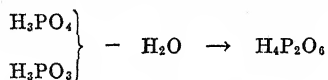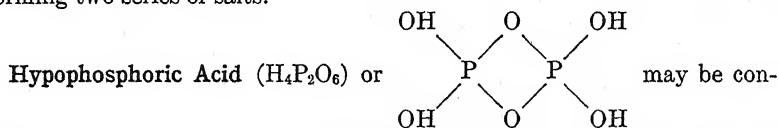
It is actually produced, however, along with phosphorous and orthophosphoric acids by the slow oxidation of phosphorus in moist air. By neutralizing the mixture of acids thus obtained with NaOH, sodium hypophosphite ($Na_2H_2P_2O_6 6H_2O$) crystallizes out of solution and may be used as the source of the free acid. With a solution of barium chloride, barium hypophosphite is precipitated and on treating this with dilute sulfuric acid, and filtering, hypophosphoric acid may be isolated, concentrated and finally crystallized at temperatures below 30°C. At 70°C this compound decom-

poses into phosphorous and phosphoric acids. The hypophosphates are used to a considerable extent in medicinal preparations.

Pyrophosphoric Acid ($H_4P_2O_7$) or

$$\text{OH}\diagdown\underset{\text{OH}}{\overset{}{P}}\overset{\text{OO}}{\diagup\diagdown}\underset{\text{O}}{}\underset{}{\overset{}{P}}\diagup\underset{\text{OH}}{\overset{\text{OH}}{}}$$
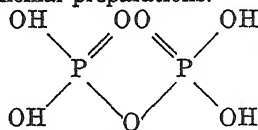
is formed

by heating orthophosphoric acid above 210°C, driving off water:

$$2H_3PO_4 - H_2O \rightarrow H_4P_2O_7$$

A certain amount of metaphosphoric acid is also formed at the same time. In order to prepare pyrophosphoric acid in a pure state it is customary to heat disodium phosphate until it is changed over into pyrophosphate, then to dissolve this salt in water and precipitate with a soluble lead compound. The lead in turn is precipitated with H_2S and the solution filtered off and concentrated in vacuum until a white crystalline mass of pyrophosphoric acid is obtained. On addition of water it readily goes back to phosphoric acid. Pyrophosphoric acid is tetrabasic but only two series of salts are known, namely, the di- and tetrabasic. These are quite stable and have some industrial significance.

Metaphosphoric Acid (HPO_3) or $\overset{\text{O}}{\underset{\text{O}}{\overset{\|}{\underset{\|}{P}}}}$—OH. **If pyrophosphoric acid is heated**
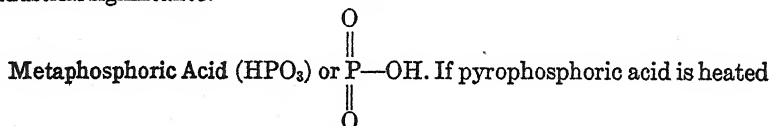
to redness water is driven off and metaphosphoric acid is formed:

$$H_4P_2O_7 - H_2O \rightarrow 2HPO_3$$

This compound may also be obtained by adding the theoretical quantity of water to phosphoric anhydride:

$$P_2O_5 + H_2O \rightarrow 2HPO_3$$

Metaphosphoric acid is a transparent glassy mass which melts at 61°C and sublimes at white heat without decomposition. It is the most stable of the oxyacids of phosphorus at high temperatures, but goes back to orthophosphoric acid when dissolved in water or exposed to atmosphere. The salts of metaphosphoric acid (metaphosphates) are formed by driving off water from the primary phosphates. On heating these compounds with water, the reverse reaction gradually takes place and orthophosphates are again produced.

Metaphosphoric acid however forms a number of salts which have the same percentage composition, but differ markedly in their properties. These are termed polymetaphosphates and are assumed to be derived from

a series of acids that are multiples of metaphosphoric acid. While these polymetaphosphoric acids themselves have not been isolated, the following is a typical series of polymetaphosphates claimed to have been prepared.

$NaPO_3$	Sodium metaphosphate
$K_2P_2O_6$	Potassium dimetaphosphate
$Na_3P_3O_9$	Sodium trimetaphosphate
$Pb_2P_4O_{12}$	Lead tetrametaphosphate
$(NH_4)_5P_5O_{15}$	Ammonium pentametaphosphate (doubtful)
$Na_6P_6O_{18}$	Sodium hexametaphosphate (doubtful)

Some of these polymetaphosphates have now assumed great commercial significance as ingredients of fertilizers[2, 11, 12], detergents[3, 6], lubricants[1] and in drilling muds[3].
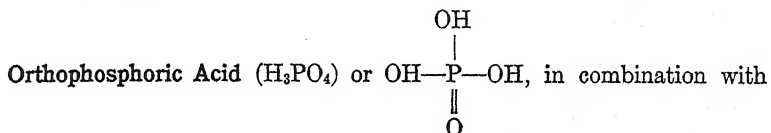
Orthophosphoric Acid (H_3PO_4) or $OH—\overset{\displaystyle OH}{\underset{\displaystyle O}{P}}—OH$, in combination with lime, is widely distributed in nature. The crystalline mineral apatite, of which two types ($Ca_5(PO_4)_3F$) and $Ca_5(PO_4)_3Cl$) exist in nature, is found as veins in igneous rocks, and from this mineral, no doubt, are derived the amorphous phosphates which are concentrated in immense deposits in various parts of the world.

Phosphoric acid is by far the most important of the oxyacids of phosphorus and the orthophosphates are used as a basis in the preparation of elemental phosphorus as well as all other phosphorus compounds.

When free from water, phosphoric acid forms colorless prismatic crystals which melt at 386°C and readily deliquesce in air. As ordinarily prepared, however, the acid is a colorless, thick syrupy liquid with strongly acid properties, (up to the point where one atom of hydrogen is replaced), readily attacking most metals with the evolution of hydrogen and the formation of the corresponding phosphate.

Orthophosphoric acid being tribasic gives rise to three series of salts as shown by following reactions:

Primary salt $H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$
Secondary salt $H_3PO_4 + 2NaOH \rightarrow Na_2HPO_4 + 2H_2O$
Tertiary salt $H_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O$
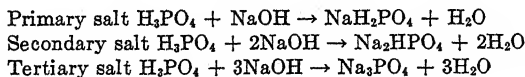
The tertiary sodium salt gives an alkaline solution, the secondary salt a solution which is slightly alkaline, while the primary salt is quite acid-to-litmus and phenolphthalein.

This behavior is due to the hydrolysis of these salts in accordance with

the following equations:

$$NaH_2PO_4 + H_2O \; NaOH + H_3PO_4 \tag{1}$$

$$Na_2HPO_4 + 2H_2O \; 2NaOH + H_2PO_4 \tag{2}$$

$$Na_3PO_4 + 3H_2O \; 3NaOH + H_3PO_4 \tag{3}$$
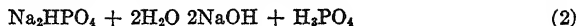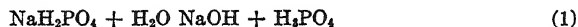
Since sodium hydroxide is a more powerful base than phosphoric acid is an acid, solutions of the normal salt act as if an excess of alkali were present, while in the case of the secondary salt the greater strength of the base is offset by the fact that the proportion of acid-hydrogen-to-base in the hydrolized solution is in the ratio of 3 to 2. Finally in the primary salts the relation of acid hydrogen to base is 3 to 1, which results in solutions distinctly acid in nature.

When heated to 300 to 400°C water is evolved and orthophosphoric acid is converted into pyrophosphoric acid ($H_4P_2O_7$). If the temperature is carried to 400°C a further quantity of water is driven off and the whole is converted into a vitreous mass of metaphosphoric acid (HPO_3).

Orthophosphoric acid may be prepared in the laboratory by dissolving phosphoric anhydride in hot water:

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

or by decomposing phosphorus pentachloride in water:

$$PCl_5 + 4H_2O \rightarrow H_3PO_4 + 5HCl$$
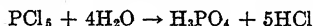
It is prepared industrially either by the action of sulfuric acid on bones or phosphate rock, or by heating mixtures of natural phosphates and silica under reducing conditions, burning the resulting elemental phosphorus to phosphorus pentoxide and hydrating this compound with water or steam. The commercial methods of preparation are discussed in Chapters 10 and 11.

Monobasic salts of orthophosphoric acid on heating lose water of constitution and are converted first into acid pyrophosphates and finally into metaphosphates:

$$CaH_4(PO_4)_2 + Heat \rightarrow CaH_2P_2O_7 + H_2O \tag{1}$$

$$CaH_2P_2O_7 + Heat \rightarrow Ca(PO_3)_2 + H_2O \tag{2}$$
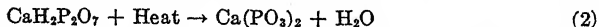
Dibasic salts of orthophosphoric acid at high temperatures also lose water and are converted into normal pyrophosphates:

$$2CaHPO_4 + Heat \rightarrow Ca_2P_2O_7 + H_2O \tag{3}$$
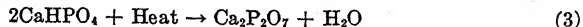
Tribasic phosphate salts undergo no change in composition when highly heated.

Phosphoric acid and its compounds have a wide application in the arts

and industries, but the greatest use is in the production of phosphatic fertilizers[3, 8].

Phosphoric Acid Terminology

The term phosphoric acid unfortunately has been, and still is used very loosely. As pointed out previously, there are at least four acids of phosphorus wherein this element is present in a fully oxidized state (hypophosphoric acid, metaphosphoric acid, pyrophosphoric acid and orthophosphoric acid), therefore, unless the particular acid of phosphorus is designated by a suitable prefix the term phosphoric acid in a strict chemical sense is entirely inadequate to express its composition.

In the fertilizer industry the term phosphoric acid refers to phosphorus pentoxide (P_2O_5). This is the unit in which the phosphorus content of the wide variety of organic and inorganic materials entering into the manufacture of fertilizers is officially expressed.

To the chemical manufacturer and distributor phosphoric acid means orthophosphosphoric acid and since this is the most useful, widely used and readily produced acid of phosphorus it is customary to drop the prefix when referring to this compound.

As a convenient common demoninator, however, the strengths of orthophosphoric acid as well as analyses of phosphate rocks and fertilizers are usually expressed in terms of P_2O_5.

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2. Phosphoric Acid in Animal and Plant Life

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Whereas this book is chiefly devoted to the sources of phosphoric acid and the methods of preparing it and its various compounds for agricultural and industrial purposes, the role that phosphoric acid plays in the life cycle of animals and plants is of the utmost concern to man.

A complete discussion of this broad subject is not within the scope of this book, but it seems fitting to give a brief resume of the vital part that phosphoric acid and its derivatives have in animal and plant metabolism.

Phosphoric Acid in Animal Metabolism

The term animal metabolism in the broader sense of the word may be used to designate the chemical changes taking place in the utilization of food by man and animals in the life process. The products of metabolism, therefore, include not only those absorbed in building up the animal body but those contained in the solid, liquid and gaseous excreta.

Metabolism includes two distinct processes, namely, anabolism by which simple molecules are built up into more complex organic compounds, and katabolism whereby the more complex compounds are broken down into simpler molecules. Since the life process is one of continual oxidation the greater tendency is toward the formation of the less complex products.

Metabolism, however, is not a simple oxidation or burning process but takes place in gradual steps in the nature of cleavages and hydrations and it is the products of these changes which unite directly with oxygen.

The role of phosphorus in animal metabolism has been so well handled by Forbes and Keith[5] (who include in their book a very complete list of references on various phases of the subject) that only a brief summary of some of the more important points is included here. For details, the reader

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is referred to the carefully prepared and excellent monograph by the authors mentioned above.

Since phosphorus in both organic and inorganic combination is an essential constituent of the bones, brain, blood, and tissue of men and animals, an adequate diet must contain sufficient quantities of this element to permit normal growth in the young and maintain the health and strength of the adult.

According to Forbes and Keith[5] the phosphorus in both animal and vegetable matter is in a highly oxidized condition and probably exists in the form of organic and inorganic compounds of orthophosphoric acid. They conclude, therefore, that there is probably no significant change in the state of oxidation of phosphorus during metabolism, although Heffter[12] observed some capacity of animals to oxidize the less completely oxidized phosphorus compounds.

Gilbert and Pasternak[8] sum up the total P_2O_5 content of the human body as being 30 to 40 grams at birth and about 1,600 grams at middle age. Of this amount 1,400 grams are contained in the bones, 130 grams in the muscles, 12 grams in the brain, 10 grams in the liver, 6 grams in the lungs and about 4 in the blood.

Table 1, compiled by Beaunis, and quoted by Forbes and Keith[5] gives the ash analyses of various animal tissues and products. The prominence of phosphoric acid in bone, muscle, brain and liver is very marked, being approximately 50 per cent of the ash of these parts.

The Coris and their co-workers[3] detected the presence of complex organic phosphates not only in the muscles, but in all animal tissues which contain glycogen. They found the formation of blood sugar in the liver could be explained by the conversion of glycogen to glucose-1-phosphate, followed by splitting the latter to glucose and inorganic phosphate by a phosphatase present. For their work on metabolic processes and the discovery of the enzyme phosphorylase which catalyzes the storage and release of sugar in the body through a phosphoric acid ester mechanism, the Coris were awarded the Nobel Prize in 1946[4]. The Eli Lilly Award in Biological Chemistry was given to Colowick for his work on the same problem[2a].

While phosphoric acid in both organic and inorganic combination is a constituent part of the animal body, this compound apparently performs certain other necessary functions in the life process independent of its absorption and retention by the bones, organs and tissues.

Loeb[19] conducted certain experiments on dogs which indicated that phosphorus is utilized in the preparation of the digestive juices. Such phosphorus may subsequently be almost entirely excreted and thus be utilized only indirectly in the building up or maintenance of the animal's health and strength.

Löb[18] demonstrated that phosphates play an important part in the digestion or utilization of sugar, and that glycolysis was favored by the presence of phosphate ions.

Forbes and Keith[5] conclude that the available data show that phosphates stand in significant relation to the digestion of food and that their excretion into the alimentary tract is of necessary consequence. Moreover, the fact that both phosphoric and sulfuric acids are prominent among the normal products of protein catabolism makes it inevitable that the excreta of man and animals contain appreciable quantities of phosphates.

Another function which phosphates play in the life process is that of helping to maintain the body fluids in a neutral or slightly alkaline state. According to Henderson[18], the phosphoric acid in such fluids is in the form

TABLE 1. ASH ANALYSES OF VARIOUS PARTS OF THE ANIMAL BODY AND ITS PRODUCTS (PER CENT)

	Bone	Calf Muscles	Brain	Liver	Lungs	Blood	Serum	Urine	Milk	Bile	Excrements
Sodium chloride....		10.59	4.74		13.0	58.81	72.88	67.26	10.73	27.70	4.63
Potassium chloride..									26.33		
Soda................		2.35	10.69	14.51	19.5	4.15	12.93	1.33		36.73	5.07
Potash..............		34.40	34.42	25.23	1.3	11.97	2.95	13.64	21.44	4.80	6.10
Lime................	37.58	1.99	0.72	3.61	1.9	1.76	2.28	1.15	18.78	1.43	26.40
Magnesia...........	1.22	1.45	1.23	0.20	1.9	1.12	0.27	1.34	0.87	0.53	10.54
Ferric oxide........				2.74	3.2	8.37	0.26		0.10	0.23	2.50
Chlorine............				2.58							
Fluorine............	1.66										
Phosphoric acid.....	53.31	48.13	48.17	50.18	48.5	10.23	1.73	11.21	19.00	10.45	36.03
Sulfuric acid........			0.75	0.92	1.4	1.67	2.10		2.64	6.39	
Carbonic acid.......	5.47					1.19	4.40			11.26	
Silicic acid..........		0.81	0.12	0.27			0.20	4.06		0.36	3.13

of mono- and disodium phosphates and mixtures of these salts in solution have greater power than any known salts for balancing either one another or any acid or base added thereto. He maintains that solutions containing these two salts will not exhibit an acid reaction until all of the disodium phosphate has been changed to the mono salt and that an alkaline reaction can only be obtained by completely converting the mono salt into disodium phosphate.

It has been established beyond question that a diet low in phosphorus compounds, or that phosphates fed under conditions which hinder their efficient utilization, bring about harmful results.

White rice, for instance, does not contain as much phosphorus as the adult requires, whereas red or unpolished rice contains more than sufficient. We store more phosphorus from whole wheat bread than from white bread.

Young flesh-eating animals suffer malnutrition of the bones if they are fed on meat alone.

The deposit of calcium phosphate in the bones is hindered by inorganic acids and acid salts as well as by calcium-precipitating ions other than phosphorus. Lime in some form along with phosphoric acid is essential for the efficient utilization of phosphorus by men and animals, but McGowan[22] says that for optimum utilization of both calcium and phosphorus after absorption, they should be supplied by food in which these two elements are uncombined with one another. He also states that the most important factor controlling absorption of phosphorus and calcium appears to be the acidity of the gastric juices.

Forbes and Keith[5], in summing up the relation of common foods to animal metabolism, state that protracted feeding of rations poor in both phosphorus and lime may seriously weaken the bones, whereas food high in these ingredients will greatly strengthen them. These authorities further state that while calcium phosphate in the diet does not greatly influence gain in body weight it is readily deposited in the bones, especially within the narrow spaces, increasing the density and strength of these supporting structures. Much time has been devoted to experiments conducted with a view to determining the relative effectiveness of organic and inorganic phosphorus in the diet of men and animals.

The fact that practically all food products (with the exception of eggs) contain both organic and inorganic phosphorus, and that bones are largely made up of phosphate of lime, led to investigations on the practicability of substituting a larger proportion of inorganic and cheaper salts of phosphoric acid for the complex and more expensive organic forms contained in certain food products.

While this problem might appear at first to be relatively simple, direct experimentation has shown that there are so many factors involved that it is difficult to draw very definite conclusions. There never has been an unanimous opinion as to the facts. It has never been definitely established that organic phosphorus is absolutely essential to animal life, nor is there proof that inorganic phosphorus can serve all the purposes for which the animal needs this element.

There is much evidence that with some species organic phosphorus compounds are more readily utilized than inorganic forms, but on the other hand, it seems likely that the many demonstrations of superior nutritive value of organic over inorganic phosphorus compounds have been influenced by other beneficial substances (such as vitamins, etc.) associated with them in natural foods or contained as impurities in the organic phosphorus compounds isolated for experimental purposes. Lowe and Steenbock[20] state that inorganic sources of both phosphorus and iron satisfy the body's need for these elements better than organic sources.

In experiments conducted to determine the relative efficiency of various

mineral supplements, Rottensten and Maynard[23] concluded that the phosphorus in dicalcium phosphate, tricalcium phosphate and in bone products was all well assimilated. Lantow[16] also states that in general monocalcium phosphate is a very satisfactory mineral food supplement for range cattle and he recommends its use.

Forbes and Keith[5] conclude that one point at least has been definitely established, namely, that an amount of organic phosphorus in food products equal to a very small part of the total is sufficient for growth and reproduction, provided the inorganic phosphorus is present in sufficient quantities to supply the balance.

TABLE 2. MINERAL ELEMENTS OF LEGUMINOUS SEEDS, NITROGENOUS CONCENTRATES AND ANIMAL PRODUCTS USED AS FEED (PARTS PER 100 OF DRIED SUBSTANCE)

Class of Feed	Potassium	Sodium	Calcium	Magnesium	Sulfur	Chlorine	Phosphorus (Total)	Phosphorus (Inorganic)	Phosphorus (Organic)
Soy beans	2.095	0.380	0.230	0.244	0.444	0.025	0.649	0.017	0.632
Navy beans	1.390	0.086	0.235	0.206	0.224	0.047	0.429	0.088	0.341
Cowpeas	1.636	0.189	0.117	0.243	0.280	0.047	0.532	0.023	0.509
Peanuts	0.061	0.563	0.068	0.180	0.254	0.024	0.399	0.049	0.350
Linseed oil meal	1.224	0.282	0.403	0.544	0.455	0.095	0.786		
Cottonseed meal	1.811	0.283	0.291	0.599	0.536	0.042	1.479	0.078	1.401
Milk (skim)	1.272	0.488	1.336	0.146	0.357	0.953	0.979	0.551	0.428
Whey	2.762	0.459	0.721	0.138	0.139	1.948	0.640	0.402	0.238
Mutton	0.624	0.214	0.006	0.062	0.607	0.235	0.474	0.230	0.244
Eggs	0.206	0.389	0.250	0.059	0.762	0.621	0.856	trace	0.856
Tankage	0.601	1.830	3.242	0.159	0.669	2.687	1.789		
Bone flour	0.065	0.091	23.990	1.160			14.940	14.940	
Blood (swine)	1.040	1.370	0.031	0.028	0.647	1.200	0.280	0.076	0.204
Black albumen	0.027	1.247	0.039	0.011	0.820	1.550	0.122	0.037	0.085

Tables 2 and 3, compiled by Forbes *et al.*[6], give the mineral constituents of certain well-known feeds and the percentage of organic and inorganic phosphorus which they contain. It will be noted that with the exception of milk products (skimmed milk and whey), malt sprouts, peanuts, and bone and tankage, organic phosphorus compounds predominate over the inorganic forms.

Unquestionably phosphate of lime is utilized by the young as well as the adult animal and certain organic wastes or by-products such as tankage, blood, bone, fish and cottonseed meal, all of which contain nitrogen and phosphoric acid, are now used extensively as stock and poultry feed. At one time such materials were used largely in the preparation of mixed fertilizers. However, it is now realized that the protein content of these products can be utilized immediately and far more economically by feeding

them directly to the animal than by breaking down this protein in the soil only to build it up again through the medium of plant life.

Most of these materials are classed as concentrated stock feeds because of their high protein content. From a fertilizer standpoint, however, such products are low grade because protein is only valued for its content of available phosphoric acid and nitrogen, both of which can be furnished

TABLE 3. MINERAL ELEMENTS OF CEREAL PRODUCTS (PARTS PER 100 OF DRY SUBSTANCE)

Grain or Its Product	Potassium	Sodium	Calcium	Magnesium	Sulfur	Chlorine	Phosphorus (Total)	Phosphorus (Inorganic)	Phosphorus (Organic)
Wheat	0.590	0.035	0.056	0.142	0.224	0.095	0.425	0.038	0.387
Wheat flour	0.058	0.127	0.022	0.019	0.168	0.081	0.102	0.017	0.085
Wheat bread	0.156	0.583	0.038	0.004	0.198	0.958	0.135	0.043	0.092
Wheat bran	1.464	0.223	0.139	0.590	0.297	1.000	1.233	0.034	1.199
Wheat middlings	1.147	0.186	0.108	0.430	0.263	0.029	0.984	0.069	0.915
Wheat germ	0.323	0.788	0.078	0.372	0.355	0.077	1.147		
Wheat gluten	0.007	0.031	0.085	0.049	1.000	0.055	0.220	0.037	0.183
Red dog flour	0.425	0.733	0.134	0.324	0.285	0.156	0.928	0.098	0.830
Corn	0.396	0.030	0.014	0.126	0.171	0.073	0.303	0.028	0.275
Corn meal (bolted)	0.192	0.113	0.015	0.122	0.122	0.070	0.264	0.019	0.245
Corn bran	0.410	0.000	0.030	0.088	0.124	0.052	0.156	0.031	0.125
Pearl hominy	0.153	0.000	0.005	0.036	0.182	0.052	0.111	0.019	0.092
Gluten feed	0.272	0.461	0.268	0.239	0.636	0.098	0.589	0.106	0.483
Distillers' grains (corn)	0.014	0.154	0.047	0.054	0.509	0.065	0.314	0.056	0.258
Distillers' grains (rye)	0.045	0.077	0.142	0.195	0.408	0.028	0.458	0.018	0.440
Brewers' grains	0.185	0.278	0.169	0.172	0.419	0.062	0.503	0.162	0.341
Malt sprouts	0.219	1.458	0.159	0.194	0.864	0.389	0.746	0.471	0.275
Oats	0.460	0.184	0.112	0.130	0.214	0.077	0.434	0.059	0.375
Kafir corn	0.288	0.066	0.013	0.142	0.186	0.117	0.271	0.012	0.259
Rice	0.040	0.032	0.009	0.028	0.114	0.040	0.104	0.003	0.101
Rice polish	1.279	0.124	0.030	0.741	0.189	0.151	1.684	0.028	1.656

more cheaply by the application of inorganic salts carrying high percentages of these ingredients.

There is very little evidence that inorganic salts of phosphorus, other than the orthophosphates, are of value in animal feeds, but steamed and degreased bone, dicalcium phosphate, precipitated tricalcium phosphate and defluorinated phosphate rock are important and valuable stock food supplements.

The treatment of ensilage with dilute phosphoric acid improves its nutrient properties, and partially or fully calcined superphosphate may

also be added to organic feed stuffs. The value of inorganic phosphorus from these various sources has been demonstrated by actual and repeated experiments, but the fluorine content of such additives should be reduced to 0.2 per cent or less to insure that there will be no deleterious effect on the stock from this latter element.

The Role of Phosphoric Acid in Agriculture

Because phosphoric acid in the main fertilizer element used in American agriculture, and the predominating ingredient of nearly all mixed fertilizers, it is rather popularly supposed that plants require larger quantities of phosphoric acid than of either potash or nitrogen. Analyses of the more common and extensively grown crops, however, as reported by a number of investigators[10, 27, 28], show conclusively that such is not the case.

In Table 4 are given the quantities of nitrogen, phosphoric acid and potash which are removed by an average crop of forage, cereals, and cotton. An inspection of this Table will show that in every instance, without exception, greater quantities of nitrogen and potash than of phosphoric acid are removed by the crops listed.

If we regard the function of phosphates as merely that of supplying phosphoric acid directly to the plant it would seem that fertilizers in which available potash and nitrogen predominate should prove much more effective in increasing crop yields than those carrying larger proportions of phosphoric acid. But when we consider the composition of typical agricultural soils from many parts of the world in respect to these three fertilizer ingredients we find that in the majority of cases their content of phosphoric acid is far less than that of potash, and frequently is considerably below their nitrogen content[7, 9, 10, 14, 15, 21, 30]. Table 5, as given by Van Slyke[29], is probably as typical as any of the average composition of good productive soils.

Not only is phosphoric acid more likely to be deficient in agricultural soils than either potash or nitrogen, but in commercial fertilizers containing readily soluble phosphates it is a well-known fact that such phosphates soon revert in the soil to less soluble compounds of phosphoric acid[2, 17, 25]. While it is generally conceded that reverted phosphates are still available to plants it is hardly to be expected that they would yield soil solutions as concentrated with respect to phosphoric acid as the original water-soluble salt.

While it must be admitted that the favorable results obtained after years of experience with materials in which phosphoric acid has predominated over both potash and nitrogen point strongly to the advisability of using fertilizers containing high proportions of P_2O_5, nevertheless, the extensive use of phosphates in this country is due in a large measure to the fact that

TABLE 4. APPROXIMATE AMOUNTS OF NITROGEN, PHOSPHORIC ACID AND POTASH IN AVERAGE YIELDS OF CERTAIN COMMON CROPS

Crop	Portion of Crop	Yields per Acre	Quantities of Fertilizer Elements Removed		
			Nitrogen (N)	Phosphoric Acid (P_2O_5)	Potash (K_2O)
			(Lbs)	(Lbs)	(Lbs)
Corn	Grain	25 bus.	23.2	9.1	5.5
	Stalks	1,500 lbs	15.0	4.5	21.0
	Cobs	250 lbs	1.0	0.2	1.1
	Total		39.2	13.8	27.6
	Green forage	20,000 lbs	60.0	26.0	66.0
Wheat	Grain	25 bus.	30.0	12.8	6.0
	Straw	2,500 lbs	12.5	3.8	15.0
	Total		42.5	16.6	21.0
Rye	Grain	20 bus.	19.1	9.8	6.7
	Straw	2,000 lbs	10.0	6.0	17.0
	Total		29.1	15.8	23.7
	Green forage	15,000 lbs	67.5	30.0	97.5
Oats	Grain	25 bus.	16.0	6.5	4.8
	Straw	1,250 lbs	8.0	2.5	15.6
	Total		24.0	9.0	20.4
	Green forage	12,000 lbs	72.0	18.0	54.0
Barley	Grain	25 bus.	21.0	9.0	6.0
	Straw	1,600 lbs	9.6	3.2	17.6
	Total		30.6	12.2	23.6
	Green forage	10,000 lbs	40.0	15.0	50.0
Buckwheat	Grain	20 bus.	15.0	6.0	3.0
	Straw	5,000 lbs	62.5	7.5	57.5
	Total		77.5	13.5	60.5
	Green forage	10,000 lbs	40.0	8.0	35.0
Cotton	Seed	550 lbs	19.3	7.7	6.3
	Lint	300 lbs	0.6	0.3	1.9
	Leaves	570 lbs	12.8	3.3	6.8
	Stalks & burrs	980 lbs	7.9	3.0	17.7
	Total	2,400 lbs	40.6	14.3	32.2
Millet	Green forage	20,000 lbs	60.0	20.0	100.0
Sorghum	Green forage	20,000 lbs	60.0	24.0	60.0

we have such immense resources of phosphate rock and for many years this fertilizer ingredient was cheaper than any other.

Laboratory, greenhouse, and field studies have shown that while phosphatic fertilizers undoubtedly furnish a certain amount of more quickly available phosphoric acid than that already in the soil they also perform a number of other important functions having both direct and indirect effects upon the soil and the crop. Soluble phosphates favor the rapid development of the young seedling by stimulating the growth of their roots, and therefore their early application often enables a plant to withstand adverse climatic conditions encountered later in the season. It is also generally believed that the liberal use of phosphates tends to hasten the early maturity and ripening of crops; an effect due to the close relationship which phosphoric acid bears to seed production[11, 28]. In climates where the crop season is relatively short, and in sections where truck is produced for early market, the quick maturity of crops is often the main factor considered and therefore

TABLE 5. PROPORTIONS OF TOTAL NITROGEN, PHOSPHORIC ACID, POTASH AND LIME IN FIRST NINE INCHES OF GOOD PRODUCTIVE SOILS

Constituent	Per Cent	Lbs in One Acre to a Depth of 9 Inches
Nitrogen (N)	0.10 to 0.30	2,500 to 7,500
Phosphoric acid (P_2O_5)	0.07 to 0.25	1,750 to 6,250
Potash (K_2O)	1.00 to 2.00	25,000 to 50,000
Lime (CaO)	0.28 to 2.10	7,000 to 52,500

success may largely depend on the liberal use of readily available phosphatic fertilizers. The tendency of phosphoric acid to increase the proportion of grain to stalk is one of its most important functions in growing cereal crops. This action of phosphoric acid is directly opposite to that of nitrogenous fertilizers, which tend to delay maturity and promote the growth of stalk and forage at the expense of the fruit. The presence of phosphoric acid is also said to be essential for the formation of chlorophyl[20]. Other effects which soluble phosphates have upon the soil, and indirectly upon the crop, are altering of the solubility of other soil constituents[1, 2], influencing the growth of soil bacteria, and nullifying the injurious effect of certain toxic organic bodies formed in the soil[26]. Also protoplasm, that essential part of both animal and vegetable life, can exist only if the plant is supplied with sufficient phosphoric acid to enable it to function properly.

Sauchelli[24] states that investigations conducted on run-down fields in France immediately after World War II established that phosphorus deficiency decreased stooling in cereal grains and therefore decreased the yields. Many of the soil types derived from granite had to be sowed to rye because they would not support a wheat crop. The results of these investi-

gations conducted by various French scientific societies to determine the deleterious effect of phosphorus deficient crops showed that inadequate quantities of phosphatic fertilizers during the war years not only caused poor yields, but the nutrient value of the harvested crops fell off to such an extent that the health and bodily functions of both animals and men were seriously impaired.

Depletion of the phosphate content of soils by erosion and the removal of crops has grown to be a matter of grave concern both in the United States and abroad and advice on combatting this menace to our agricultural security is being widely distributed through state and federal agricultural agencies. As a consequence, farmers are adopting more rational systems of cultivation and cropping to check erosion losses and are restoring and building up the fertility of their soils by the more liberal use of fertilizers.

RADIOACTIVE PHOSPHORUS: ITS USE IN SOIL AND FERTILIZER STUDIES*

In this atomic age the utilization of radioisotopes or "tagged" atoms in the development of new techniques for the study of soil and plant nutrition problems has been foreshadowed by the success of isotopes in medical research. The remarkably sensitive Geiger-Müller counter, able to detect radioactive tracers in substances only a billionth gram in weight, became an indispensable adjunct in these new research techniques.

A radioisotope or radioactive tracer is a substance which having been exposed to intense radiations within a nuclear chain-reacting pile or atomic furnace becomes radioactive itself. This simply means that the substance sends off invisible radiations whose paths can be traced by means of sensitive instruments. These radioisotopes are a direct product of atomic energy development. The Atomic Energy Commission at Oak Ridge, Tennessee, has made it possible for many research agencies to obtain these radiated substances for peacetime studies.

According to this new method of study, tagged atoms may be incorporated into a plant food carrier, such as superphosphate, and placed in the soil. Then, by means of the Geiger counter, their course can be charted as they travel through the tissues of the growing plant which absorbs them, the length of time they remain there, and their eventual disposition by the plant. In other words, radioisotopes furnish us a tool for exploring, for the first time, the inner secrets of plant nutrition at the root-tip-clay surface area and within the plant tissues.

Radiophosphorus was one of the earliest radioisotopes to be produced in large quantities. It has proved very useful and convenient, particularly since it is relatively inexpensive and has a half life of 14.3 days. This means that half of the radioactivity is lost every 14 days until at 114 days only

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$\frac{1}{256}$ of its original intensity remains. Since 1946 the U. S. Department of Agriculture in cooperation with several state agricultural stations has organized and supervised a research project sponsored jointly by the fertilizer industry and the government to study the profitable use of phosphorus in various forms on different soils and with different crops. In this project radioactive phosphorus is converted to a suitable phosphatic fertilizer along with inactivated phosphate. It is an important basic consideration that radiophosphorus has the same chemical properties as inactive phosphorus, and both kinds of phosphorus will behave identically in all reactions and will travel the same path. The quantity of tagged phosphorus a root tip absorbs in a few minutes can be measured by the new technique even though the amount is less than one-millionth of a gram. Another advantage not possible with chemical determinations is that a tagged substance can be distinguished from an untagged material of the same substance. Hence, it is now possible to segregate the absorbed phosphate or other tagged element in the applied form from the same untagged element present in the soil. The fate of tagged fertilizers can be determined both in the soil and in the plant tissues, and the tracing of the tagged element can be done on the living plant without in any way interfering with its normal functions. This obviously is a real and valuable advantage of the tracer technique. Actually the method followed is this: when the plant has reached the desired stage of growth it is collected, ashed, and the radioactivity of the ash measured by the Geiger counter. From this the fertilizer uptake is calculated. The total amount of phosphorus taken up by the plant is determined by chemical analysis. Then, by subtracting the amount of applied phosphorus as calculated by means of the Geiger counter from this total, the amount of phosphorus derived from the soil is obtained. The usual chemical method of determining the amount of applied phosphorus absorbed by the crop is to subtract the amount of phosphorus uptake in the check plots from that determined for the fertilized plots. The radioactive phosphorus method is obviously superior, since by means of it one can segregate the applied from the native soil phosphorus uptaken.

It is too soon to permit more than a provisional evaluation of this new technique. Hardly five years have elapsed since these tracers were first used on a large scale. The technique is spectacular and has aroused great expectations. It is the consensus of competent opinion at this time that the technique is the most direct approach to many plant nutrition and biological problems, and offers the opportunity of studying the fixation of phosphorus in the soil, the uptake of phosphorus by the plant, and the relative efficiency of various types of phosphatic fertilizers. Time will tell how effective this new tool may become in the solution of phosphate production problems in the fertilizer works.

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3. Sources of Phosphoric Acid and Their Classification

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No very strict line can be drawn between soluble and insoluble phosphates, between available and unavailable forms of phosphoric acid, or even between natural and manufactured phosphatic fertilizers. Nevertheless, for convenience, the following three broad classifications are made, based partly on the relative solubility of such phosphates and partly upon their mode of occurrence and their chemical and physical properties:

(1) The natural phosphates including raw bone, guano, apatite and phosphorite or phosphate rock. All of these, with the exception of certain types of guano, are nearly insoluble in water and are slowly available under soil conditions.

(2) The so-called available phosphates which are the products or by-products of various industrial processes. These phosphates very sparingly soluble in water but dissolve readily in certain conventional laboratory solutions. They include steamed or degreased bone, basic slag, dicalcium phosphate, defluorinated phosphate rock, calcium metaphosphate and a number of manufactured materials which yield phosphoric acid upon treatment with neutral ammonium citrate solution.

(3) Water-soluble phosphates or those which dissolve most readily and as a rule have the quickest effect upon crop yields. The chief fertilizer products under this classification are ordinary superphosphate, triple superphosphate and ammonium phosphates, all of which are main products of industrial processes.

In addition, there are the pure water-soluble salts such as monocalcium phosphate and the phosphates of the alkali metals used for purposes other than fertilizers.

The phosphoric acid content of typical phosphate materials, natural and manufactured, are given in Table 1.

The Natural Phosphates

The natural or relatively insoluble phosphates represent the raw materials

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TABLE 1. COMPOSITION OF NATURAL AND MANUFACTURED PHOSPHATES USED DIRECTLY OR INDIRECTLY IN AGRICULTURE

Phosphatic Material	Source	Nitrogen (N)	Silica or Insoluble (SiO_2)	Oxide of Iron and Aluminum ($Fe_2O_3 + Al_2O_3$)	Calcium Fluoride (CaF_2)	Carbonate of Lime ($CaCO_3$)	Phosphoric Acid (P_2O_5)	Tricalcium Phosphate ($Ca_3(PO_4)_2$)	Potash (K_2O)
Natural Phosphates									
Apatite	Bohemia		3.7 to 8.9	0.7 to 1.0	5.26	8.54	30.59	66.79	
Apatite	Canada				3.0 to 7.3	0.0 to 8.0	34.1 to 40.0	78.6 to 86.8	
Apatite	Norway		3.62	1.37	2.62	0.29	39.44	86.10	
Coprolites	Bohemia								
Coprolites	France		3.00				6.99	15.25	
Coprolites	Great Britain			6.0 to 17.0					
Guano	S. Africa	1.4 to 8.9		4.4 to 13.0	3.0 to 6.0	2.3 to 24.0	12.0 to 21.0	26.3 to 46.0	
Guano	S. America	1.3 to 14.4		3.25			15.4 to 34.0	33.6 to 77.7	
Guano	Australia			1.0 to 2.0			11.2 to 24.5	24.4 to 55.4	
Guano (bat)	Italy	7.54		0.97		0.0 to 14.0	9.8 to 17.5	21.3 to 38.3	
Guano (bat)	Porto Rico	5.72		trace		6.97	7.30	15.94	
Guano (in crusts)	Sporadic Isles	8.35		1.59			5.02	10.95	
Guano (in crusts)	W. Indies	0.45					7.57	16.52	
Guano (phospho)	S. Africa	0.43					40.12	87.58	
Guano (phospho)	Asia	0.8 to 1.4		0.4 to 9.3		6.23	6.68	14.60	
Guano (phospho)	Australia	0.4 to 1.3					24.4 to 40.5	53.2 to 60.8	
Guano (phospho)	Pacific Ocean Isles	0.3 to 1.3		1.48	trace to 2.6	4.3 to 4.6	26.2 to 31.2	57.3 to 68.0	
Guano (phospho)	Mexico & West Indies	0.1 to 0.4		0.8 to 3.1	0.8 to 1.0	4.5 to 16.5	23.6 to 35.2	51.4 to 76.9	
Phosphatic chalk	Belgium			0.2 to 0.3		3.8 to 12.8	17.7 to 40.3	38.6 to 88.0	
Phosphorites	Algeria (Afr.)		1.2 to 2.6	trace to 5.8		7.04	11.6 to 39.7	25.3 to 86.7	
Phosphorites	Morocco (Afr.)		6.0	2.4 to 2.9		0.0 to 22.8	22.2 to 27.3	48.4 to 59.5	
Phosphorites	Tunis (Afr.)		3.0 to 9.9	0.5 to 1.0		6.4 to 10.0	26.3 to 30.4	57.4 to 66.4	
Phosphorites	Egypt (Afr.)			0.7 to 1.6	5.2 to 9.4	11.5 to 14.0	32.8 to 35.2	71.6 to 76.7	
Phosphorites (white)	Christmas Isle (Asia)			1.0 to 2.0	6.6	9.3 to 11.3	27.5 to 31.2	60.0 to 68.0	
Phosphorites	Ocean Isle (Pacific)			1.0 to 2.3			28.0 to 32.9	61.2 to 71.8	
Phosphorites	Podolia (Russia)			1.93	3.44	4.82	39.20	83.53	
Phosphorites	Somme (France)			0.42	1.00	4.91	38.73	84.65	
Phosphorites	Spain			2.21		6.92	32.25	74.23	
Phosphorites, black rock	Arkansus (U.S.)		15.0 to 40.0	1.3 to 2.2	1.0 to 14.0	9.10	29.5 to 38.9	59.6 to 85.0	
Phosphorites, hard rock	Florida (U.S.)		4.13	2.5 to 9.5		10.3 to 13.3	36.39	83.14	
Phosphorites, land pebble	Florida (U.S.)		5.0 to 10.0	3.0	4.4	3.63	30.0 to 34.0	69.0 to 78.0	
Phosphorites, soft phosphate	Florida (U.S.)			1.0 to 4.0	0.0 to 3.0	2.0 to 5.0	25.0 to 27.0	54.5 to 58.8	

Material	Source							
Phosphorites, brown rock	Kentucky (U. S.)		2.0 to 5.0	2.5 to 5.0	2.0 to 8.0	11.0 to 25.0	30.0 to 35.0	69.0 to 80.0
Phosphorites, nodules	S. Carolina (U. S.)		4.0 to 12.0	1.0 to 4.0	0.0 to 5.0	0.0 to 10.0	25.0 to 28.0	57.0 to 64.0
Phosphorites, brown rock	Tennessee (U. S.)		2.5 to 10.0	3.0 to 8.0	0.0 to 3.0	0.0 to 10.0	30.0 to 38.0	69.0 to 87.0
Phosphorites, blue rock	Tennessee (U. S.)		2.5 to 7.0	2.5 to 7.0			27.0 to 32.0	62.0 to 73.0
Phosphorites, white rock	Tennessee (U. S.)		2.0 to 7.5	1.5 to 3.5			32.0 to 38.0	73.0 to 87.0
Phosphorites, oolitic black	Utah, Idaho etc. (U. S.)		1.8 to 10.0	0.7 to 1.6	0.8 to 1.4	3.8 to 13.6	27.0 to 36.5	62.0 to 83.0
So-Called Available phosphates								
Fresh bone	By-product	4.00				5.00	22.30	48.70
Bone ash	By-product	4.14	3.01			5.28	35.38	76.65
Bone (fat extracted)	By-product	1.12	3.60	0.37		5.24	21.68	46.50
Bone or animal charcoal	By-product	8.20	2.00		1.00	8.00	31.99	73.10
Tankage (high grade)	By-product	5.00					3.70	
Tankage (low grade)	By-product						11.40	
Basic slag	By-product						18.0 to 20.0	
Fish scrap	By-product	8.80					8.0 to 9.5	
Calcined (defluorinated phosphate)	Manufd.		2.0 to 5.0		0.01 to 0.1		20 to 30	
Calcium metaphosphate	Manufd.		2.0 to 5.0				60 to 65	
Dicalcium phosphate	Manufd.						40.0	
Rhenania phosphate	Manufd.						23 to 25	
Water-Soluble Phosphates								
Ammon. phosphate (mono)	Manufd.	10.0					55.0	
Ammon. phosphate (di)	Manufd.	20.0					50.0	
Ammophoska I	Manufd.	12.0					24.0	
Ammophoska II	Manufd.	10.0					20.0	12.0
Ammophoska III	Manufd.	17.0					30.0	15.0
Nitrophoska I	Manufd.	17.5					13.0	10.0
Nitrophoska II	Manufd.	15.0					11.0	22.0
Nitrophoska III	Manufd.	16.5					16.5	26.5
Calcium phosphate (mono)	Manufd.						52.0	21.5
Potass. phosphate (mono)	Manufd.						52.0	34.0
Potass. metaphosphate	Manufd.						60.0	34.0
Sodium phosphate (mono)	Manufd.						50.0	40.0
Sodium phosphate (di)	Manufd.						19.8	
Sodium phosphate (tri)	Manufd.						18.7	
Superphosphate	Manufd.		2.0 to 5.0		2.0 to 4.0		18 to 20	
Triple superphosphate	Manufd.		1.0 to 2.0		1.0 to 2.0		40 to 48	

from which the plant must draw its phosphoric acid, whether they are applied in their natural state directly to the soil with very little preliminary preparation, or so manipulated in the factory as to yield phosphatic compounds of entirely different composition. From the natural phosphates are also produced elemental phosphorus, the acids of phosphorus and the various salts of phosphoric acid which are annually coming to have a greater commercial significance and wider industrial applications.

Whereas finely ground (but otherwise untreated) natural phosphates undoubtedly have an agricultural value and are still used for fertilizer purposes to a limited extent, most of them are generally regarded as inferior to the factory manipulated phosphates, the nature of which has been altered by the application of high temperature or treatment with various chemical reagents.

Bones and Bone Products

The first use of raw or green bone for fertilizer purposes is so ancient as to be lost in antiquity. Long before their composition was suspected they were used in their natural state (frequently not even crushed) to increase crop yields. Later, when the fertilizer value of phosphoric acid was established and the nature of bones determined by chemical analysis, the demand for bones became so great that old battlefields were plowed up and ancient cattle ranges sought for what was then considered one of the most valuable of phosphate fertilizers.

While raw bones differ considerably in composition, depending on the source, age and natural agencies which have been at work upon them, as ordinarily collected they contain from 20 to 22 per cent of phosphoric acid (P_2O_5) and from 5 to 7 per cent of nitrogen.

The term raw bone, however, is rather indefinite since it includes not only bones from recently slaughtered animals but also those which have been weathered or buried for long periods of time. Both the nature and agricultural efficiency of these two extremes differ greatly and large quantities of bones are now seldom purchased without knowing their source and chemical composition.

In addition to large amounts of water, fresh or green bones contain over 40 per cent organic matter, part of which is of such a character as to delay considerably the decomposition of the bone under soil conditions. The approximate composition of such bones is as follows:

	(%)
Moisture	34.00
Mineral matter (ash)	23.00
Fats	20.00
Albuminoids	21.00
Undetermined organic matter	2.00

The mineral matter or ash of average bone has the following composition:

	(%)
Calcium phosphate $(Ca_3(PO_4)_2)$	87.00
Calcium carbonate $(CaCO_3)$	12.00
Silica (SiO_2), Fluorine (F), etc.	1.00

The albuminoids in bone consist chiefly of ossein, a gelatinous material containing nearly 18 per cent of nitrogen, and valuable for the manufacture of glue. While the albuminoids decompose or putrefy very readily when moistened, their presence in fresh bone renders the latter very difficult to grind. The fat or grease in fresh bones, on the other hand, retards their decomposition in the soil and hence lessens their value for agricultural purposes. Raw bones which have been weathered contain far less moisture and organic matter than fresh bone and as a rule can be much more readily ground. The availability of the P_2O_5 contained therein, however, is not as high as that in processed and degreased bone which are discussed in detail in Chapter 19.

Bone charcoal and bone ash hardly belong under the classification of natural phosphates because they have been processed to a certain extent by artificial means. As far as their agricultural availability is concerned, however, they should be included among the relatively insoluble phosphates since they show a solubility in conventional media but little greater than that of finely ground phosphate rock.

The former material (bone charcoal) is the residue remaining after bones have been submitted to destructive distillation in air-tight retorts and the volatile constituents driven off or decomposed. The organic matter which remains is largely carbon. Bone black is produced primarily for the purification and clarification of oils and sugar juices, and only after its activity for these purposes is largely spent does it enter into the fertilizer industry. Its solubility in water and citrate solutions is very slight and while the nitrogen which it takes up in the purification of sugar adds somewhat to its value as a fertilizer, the general practice is to treat spent bone black with sulfuric acid and convert its P_2O_5 into a water-soluble form. Bone black varies greatly in composition depending on how often it has been used and revivified. In Table 2, Fritsch[9] gives the analyses of several samples of bone black before and after being used in the refining of sugar. The manufacture, use and revivification of bone black is treated more fully in Chapter 27.

Bone ash is merely the mineral matter which remains after bones have been burned for fuel. At one time large quantities of this ash were shipped to the United States and Europe from certain South American countries. The immense prairies in Argentine, for instance, support vast herds of cattle and a century or more ago these animals were often slaughtered

merely for their skins, horns and fat. According to Fritsch the flesh was seldom used for human food but the bones were consumed for domestic fuel. As a result great mounds of bone ash accumulated, although the value was not appreciated until many years later. When the importance of this high grade phosphate was recognized, however, the bone ash was hauled to the seaboard and shipped to foreign countries where it was used for manufacturing very high grade superphosphate and pure phosphate products.

TABLE 2. ANALYSES OF FRESH, USED AND SPENT BONE BLACK

Description of Material	Nitrogen (%)	Carbon and Org. Mat. (%)	Phosphate of Lime (%)	Carbonate of Lime (%)	Other Constituents (%)
Charcoal					
fine, new	1.12	11.6	73.1	8.0	7.3
once used	1.95	21.1	64.6	6.4	7.9
fine, new	1.22	11.3	72.2	5.3	10.5
once used	2.83	32.0	53.7	4.9	9.4
twice used	3.59	42.2	46.0	3.3	8.5
fine, new	1.61	11.0	75.6	7.0	13.4
once used	2.54	36.2	52.6	10.0	10.1
twice used	3.18	42.5	47.5	4.5	5.2

TABLE 3. CHEMICAL COMPOSITION OF FIVE TYPICAL SAMPLES OF BONE ASH

Sample No.	1 (%)	2 (%)	3 (%)	4 (%)	5 (%)
Moisture and organic matter	8.89	19.66	17.37	3.39	10.30
P_2O_5	35.38	33.89	32.63	38.12	29.56
CaO	47.80	43.00	39.76	48.92	35.50
MgO	0.97	0.97	1.48		
Na_2O, K_2O		1.39	0.84	5.67	4.40
Fe_2O_3	3.01	0.78	0.21		
CO_2			0.84		
SiO_2	6.95	8.31	6.50	3.90	20.24

This material is now nearly exhausted and the ancient practice of burning bones and thus destroying much of their commercial value is recognized as a profligate waste. Bone ash, however, is a very high-grade raw phosphate material and finds a ready market where relatively concentrated or pure phosphate products are manufactured. The analyses of typical samples of bone ash (Table 3) show how free most of this material is from objectionable impurities.

Guano

The word guano is derived from the Peruvian word "huanu" meaning excrement. It is the oldest fertilizer known to man, for literature shows

that the excrements of birds and animals were used for agricultural purposes at least 200 years B.C. While there appears to have been a period during which the fertilizer merits of guano were unappreciated or forgotten in certain European countries, it again came into use in 1840[1] when a firm of Lima merchants sent a cargo of Peruvian guano to London. Twenty-two years later (1862) the annual exports of guano from Peru had risen to 435,000 tons.

Although guano occurs in natural deposits it cannot be properly classed among the relatively insoluble phosphates since its composition and agricultural availability vary widely depending upon the source of the materials, the conditions under which it has been laid down, and the natural agencies to which it has been exposed[10].

The guano deposits found in arid regions or in caves (bat guano), where the material has not been subjected to the leaching action of water, contain, as a rule, phosphoric acid in a much more soluble and available form than the guano which has been leached by percolating waters. The former material also contains, in addition to the phosphoric acid, considerable amounts of nitrogen, which greatly increases its commercial value. Between the two extremes of guano containing nearly all of its original organic matter, and that which has been so weathered as to resemble phosphate rock, there are many deposits in various stages of decomposition. Most of the guano entering the fertilizer market comes from India, Africa, the West Indies, Argentine, and certain islands off the Coast of Peru. It is chiefly derived from the accumulation in caves where great numbers of bats congregate or from the droppings of birds which feed upon fish and marine animals. Because of the great variation in the composition of guano it is seldom purchased without the buyer knowing definitely the percentages of nitrogen and phosphoric acid (both available and insoluble) which it contains.

The most famous deposits of guano are those occurring on certain groups of islands off the coast of Peru[6] where for thousands of years vast numbers of fish-eating birds have nested and reared their young. The dung and remains of countless generations of these marine birds have accumulated in guano beds which have reached a thickness in certain places of over 100 feet.

These deposits probably represent the most valuable natural fertilizer known since they occur in a rainless region and have retained nearly all of their soluble constituents. It is true that large guano deposits derived from the same source (the dung of marine birds) are found upon islands in the Caribbean Sea, upon the coast of Africa, and on other islands of the Pacific Ocean, but practically all of these deposits occur in humid regions where the rainfall has leached away much of their nitrogen content leaving a residue of the less soluble phosphates. Such residues and the phosphatized

underlying lime rock constitute some of the highest grade phosphate deposits in the world.

The nitrogen content of Peruvian guano, however, seldom falls below $8\frac{1}{2}$ per cent and will often run as high as 16 per cent. This material, therefore, is valued chiefly as a nitrogenous fertilizer although it contains a high percentage of phosphoric acid (much of which is citrate soluble) and appreciable quantities of potash.

At one time these guano deposits constituted an important source of revenue to the Peruvian government. For years their exploitation was carried on so indiscriminately and with so little regard for the future that they have been very much depleted and it finally became evident that they would soon be exhausted unless steps were taken to conserve them and protect the birds from which they were derived. According to Coker[6] more than 10,000,000 tons of Peruvian guano valued at from $400,000,000 to $600,000,000 were extracted and shipped from one small group of islands between 1851 and 1872.

About this time, however, laws were passed limiting the exports of guano, and later regulations were adopted whereby the islands were mined in rotation and the extraction of guano restricted so as to interfere as little as possible with the birds, particularly while they are breeding. In this way the supplies of guano are being replenished to a certain extent but at a rate hardly more than sufficient to meet the demands of domestic agriculture. Coker[6] found that in certain rookeries where the birds were left unmolested the guano accumulated at the rate of $4\frac{1}{2}$ inches per annum or 300 pounds to the square yard. This annual deposition seems almost incredible until one considers that some of these marine birds consume as much as 8 to 10 pounds of fish each day. Their nests are frequently built so close together that they resemble eggs in a crate.

Bat guano is another type of natural nitrogenous phosphate fertilizer but it does not compare in value to Peruvian guano. The deposits are much smaller, the annual accumulations far less (due to the relatively small quantities of food consumed by bats), and the caves in which the material is deposited are frequently so isolated that it hardly pays to exploit them. Moreover, the composition of bat guano varies greatly not only in different caves but in different parts and at various depths of the same caves depending upon the amount of percolating water entering the cave, the intrusion of soil or other foreign material, the type of rock forming the base of the cave, and the character of the bacterial activities which function under different conditions. Gile and Carrero[11] made a thorough examination of a large number of samples of bat guano from various parts of Porto Rico and found that the nitrogen content of this material ranged all the way from an almost negligible amount to 13.04 per cent and the phosphoric acid (P_2O_5) from less than 1 per cent to 41.58 per cent.

Most guano, even that which has been largely leached of its more soluble constituents, is ground and applied directly upon the field, although some is treated with sulfuric acid and its fertilizer constituents thereby rendered more soluble and quickly available to crops.

Apatite

Apatite is a phosphate mineral having a crystalline structure (hexagonal) and a more or less definite chemical composition. Two varieties occur in nature, namely, chloroapatite $Ca_5(PO_4)_3Cl$ and fluorapatite $Ca_5(PO_4)_3F$[4, 12]. These two types when pure contain from 40.9 to 42.26 per cent of P_2O_5, which is a higher phosphoric acid content than any other phosphate mineral found in large deposits. Hydroxyapatite $(Ca_5(PO_4)_3OH)$, in which the OH radical replaces F, is formed when phosphate rock is calcined or defluorinated at high temperatures and allowed to cool slowly. All forms of apatite are very sparingly soluble in pure water.

While widely distributed in nature, apatite occurs chiefly as veins or intrusions in igneous rocks and therefore is probably derived directly from the molten magma. It has been prepared synthetically in the laboratory by a number of investigators both from mixtures of highly heated or fused materials[8, 17] and by heating said mixtures with water under pressure[3, 7].

It is generally conceded that apatite is the original source of P_2O_5 in the soil, as well as of practically all natural commercial phosphates. Since it is appreciably soluble in carbonated waters some of the mineral is constantly carried to the sea where it is absorbed and concentrated by living organisms. Some portions react with other products of rock decomposition forming new secondary phosphates which may be subsequently segregated in relatively large deposits; other portions enter the soil and are taken up by plants which in turn may be either consumed by men and animals, and the phosphoric acid thus utilized to build up bone and tissue, or the phosphate may be again returned to the soil in the form of excrements and as residues resulting from death and decay of vegetable life.

Although sometimes found in large bodies, apatite like nearly all mineral veins or intrusions often is very irregular in occurrence. The world's largest and most important deposits of apatite are located on the Kola Peninsula, near Kirovsk, U. S. S. R. The rock is found in great lenses between two types of alkalic rocks. The apatite is in granular aggregates intimately associated with nepheline. These deposits are the only ones now being actively exploited[20].

Deposits of apatite also occur in Norway, Spain and Canada and before the discovery of the immense deposits of amorphous phosphates in the United States the mining of Canadian apatite was conducted on a fairly extensive scale[26]. The peak of production in Canada was reached in 1890 when the annual output amounted to 31,753 tons. Since that date the in-

dustry has steadily declined and as early as 1896 the annual production had fallen to 570 tons.

Large reserves of apatite still remain in the provinces of Ontario and Quebec[22] but the small tonnage which enters the market is obtained merely as a by-product in the mining of mica with which the apatite of the latter province is associated. The irregularity and uncertainty of these vein deposits and the hardness of the country rock make the cost of prospecting and mining apatite relatively high. Moreover, the material must be cobbed or hand picked in order to insure a high-grade product, which adds further to the final cost. It is a significant fact that three of the countries mentioned above have not only ceased to export apatite but practically all of the phosphatic fertilizer manufactured for domestic use is produced from amorphous phosphate rock imported from Africa or the United States.

Phosphorite or Phosphate Rock

Phosphorite or amorphous phosphate rock which occurs in sedimentary deposits (usually of marine origin) in many parts of the world is by far the most important of the raw materials used as sources of phosphoric acid for fertilizer and other industrial purposes.

Jacob[13] found that nearly all deposits of phosphorite contain F and P_2O_5 in the same ratio as they occur in apatite. The presence of fluorine as a constituent part of the calcium phosphate molecule is responsible for the low solubility of the P_2O_5 and accounts for the accumulation and preservation of these phosphate deposits[18].

Few minerals marked today are found at a greater number of geologic horizons and occur under a wider range of natural conditions than phosphate rock. It is found in deposits of Ordovician, Silurian, Devonian and Carboniferous Age, in Jurassic, Cretaceous, Tertiary and even more recent strata. Its physical properties vary all the way from hard flint-like masses to soft plastic material resembling kaolin, and from black massive seams of rock which have been mistaken for coal to brown, porous thin-bedded strata or to small white nodules and pebbles. Some deposits show little evidence of organic origin while others contain fossilized bone, teeth and the waterworn casts of phosphatic shells.

While different deposits, as well as the several strata in the same deposit may vary considerably in value and extent, phosphate rock on the whole is readily and cheaply mined, and there is little doubt that the abundance and low cost of this mineral are largely responsible for the expansion of the fertilizer industry and the economic maintenance and increase in crop yields.

The ratio of lime to phosphoric acid in the purest samples of phosphorite approaches that in fluorapatite ($Ca_3(PO_4)_3F$) or tricalcium phos-

phate $(Ca_3(PO_4)_2)^5$, but nearly all phosphate rock contains as impurities various amounts of organic matter, iron and aluminum oxides or phosphates, carbonates of lime and magnesium and fluorine compounds. Moreover, nodular, pebble and plate phosphates are usually found mixed with clay and sand from which they must be separated by washing, gravity and flotation processes. In the case of the bedded deposits the rock may be interstratified with limestone and shales entailing selective mining in order to obtain a marketable product.

The phosphate rock deposits of the world in the order of their present commercial importance are as follows: the phosphates of the United States including those of great value and extent in Florida, Tennessee, and the western states, Utah, Idaho, Wyoming and Montana and deposits of less importance in South Carolina, Kentucky, Virginia and Arkansas; the deposits of northern Africa in Algeria, Tunis, Egypt and Morocco; the apatite deposits of the Kola Peninsula, U. S. S. R.; the deposits in the Pacific and Indian Oceans including those of Ocean, Christmas and Nauru Islands, and islands of the Marshall, Pellew and Society groups; deposits of less importance in Australia, Japan and New Zealand; the phosphates of Belgium, France, England; and a number of smaller deposits in various other countries.

Finely Ground Raw Rock Phosphate

In order to maintain the fertility of soils indefinitely with respect to phosphoric acid, a number of agronomists and agricultural chemists recommend the application of finely ground unacidulated raw rock phosphate directly on the field. A considerable tonnage is thus annually used. From a strictly theoretical standpoint it would appear that finely ground raw rock phosphate should be an effective phosphate carrier, particularly when applied to soils low in P_2O_5. The mineral phosphates of the soil which normally support plant life probably have no greater solubility than phosphate rock. In fact, iron and aluminum phosphates, often the chief compounds of phosphoric acid in soils, are no more soluble than phosphate rock, which is known to be appreciably dissolved by carbonated waters and therefore should enter the soil solution which is nearly always rich in carbon dioxide.

The agricultural value of finely ground unacidulated mineral phosphates does not lack practical supporting evidence. Many experiments conducted in the laboratory greenhouse and field point strongly to the merit of this material and a compilation and classification of many long-time experiments conducted with raw rock phosphate[24] led to the conclusion that this material usually increased crop yields. From a financial standpoint the results obtained often compared favorably with those from other types of

TABLE 4. WORLD PRODUCTION OF PHOSPHATE ROCK BY COUNTRIES, 1939–1949, IN METRIC TONS

Country[1]	1939	1940	1941	1942	1943	1944	1945	1946	1947	1948	1949
Algeria	450,000	370,890	446,535	334,550	76,798	220,349	401,304	584,827	706,878	670,591	645,906
Australia:											
New South Wales	(²)	20	31	118	122	(²)	725	20	231	(²)	(²)
South Australia		254	8,570	14,182	12,976	4,187	8,619	(²)	5,171	(²)3,500	(²)
Western Australia	17	39	21	43	43	2,251	(²)	(²)	(²)	(²)	(²)
Austria	(²)	(²)	(²)	(²)	(²)	(²)	(²)	3,240	11,625	(²)	(²)
Belgium	(²)	280	36,660	103,300	108,900	52,270	17,990	(²)	58,045	68,938	(²)
Brazil (apatite)	(²)	(²)	(²)	(²)	6,111	5,216	7,463	10,421	5,592	(²)	44,643
British West Indies:											
Cayman Islands	(²)	(²)	(²)	203	102	(²)	(²)	(²)	(²)	(²)	(²)
Canada	142	325	2,256	1,147	1,316	437	271	52	(²)	(²)	4,553
Chile (apatite)	9,014	32,000	29,123	24,909	37,924	50,840	13,203	15,210	13,994	59,529	11
Christmas Island	177,972	241,826	111,708	(²)	(²)	(²)	6,096	34,444	106,765	108,311	255,236
Egypt	547,638	183,464	(²)	328,440	315,566	318,185	349,374	294,046	371,227	377,005	350,000
Eire	(²)	(²)	(²)	16,444	17,252	20,300	(²)	12,189	(²)	(²)	(²)
France	(²)	24,260	98,660	113,400	131,020	92,996	60,622	88,924	56,786	(²)	(²)
French Oceania (exports)	160,680	164,170	192,235	176,065	188,385	203,300	259,000	241,000	205,136	183,104	239,532
Germany	(²)	1,548	1,043	829	585	(²)	(²)	(²)210	698	473	(²)
India	185	119	81	337	1,215	232	532	247	887	(²)	(²)
Indochina, French:											
Phosphate rock	35,694	24,340	40,310	29,050	19,890	6,850	(²)	(²)	(²)	(²)	(²)
Apatite	(²)	2,070	30,800	98,800	64,600	300	(²)	(²)	(²)	(²)	(²)
Italy	(²)	274	1,300	1,400	1,200	(²)	2,000	(²)	(²)	(²)	(²)
Japan	6,600	1,400	(²)	(²)	(²)	3,000	(²)	(²)	(²)	3,600	(²)
Madagascar	(²)	495	(²)	(²)	(²)	(²)	(²)	(²)	(²)	(²)	684
Morocco, French	1,702,973	687,310	493,060	715,410	806,171	1,444,902	1,654,120	2,783,800	2,960,727	3,226,326	3,693,000
Nauru & Ocean Islands	1,244,170	1,263,385	(²)	(²)	(²)	(²)	(²)	(²)	224,039	480,562	1,067,157
Netherlands Indies	18,777	34,085	(²)	(²)24,000	(²)24,000	(²)24,000	(²)	(²)	(²)	(²)	(²)
Netherlands West Indies:											
Curaçao (exports)	64,072	6,047	111,905	(²)	9,389	7,812	8,770	11,224	(²)	(²)	(²)
New Zealand	(²)	(²)	—	(²)	(²)5,384	20,251	8,084	(²)	(²)	68,827	92,784
Palestine	(²)	95	(²)	2,818	1,849	(²)4,961	(²)4,887	(²)4,024	203	(²)	(²)
Rumania	(²)	(²)	2	(²)	(²)	(²)	(²)	(²)	(²)	(²)	
Seychelles Islands (exports)	23,545	14,613	18,795	22,347		5,941	7,090	21,397	1,516	21,924	14,243
South-West Africa		869	(²)	59	164		27	1,665	2,223	1,038	957

Spain (apatite)	10,320	15,781	13,846	15,232	15,722	17,770	20,349	18,608	21,651	23,012	23,093
Sweden (apatite)	6,267	7,479	31,116	79,305	144,265	160,847	171,127	50,730	[2]	[2]	[2]
Tanganyika Territory	132	9	33	25	267	28	9	279	[2]	313	157
Tunisia	1,627,912	1,187,823	1,076,118	879,743	334,678	522,265	706,404	1,399,880	1,759,236	1,863,710	1,441,918
Uganda	[2]	[2]	[2]	[2]	[2]	[2]	8,648	7,213	7,269	[2]	[2]
Union of South Africa	[2]	[2]	425	9	5,801	21,088	27,342	37,643	41,331	39,656	56,471
U. S. S. R. (apatite)	[2]	2,600,000	2,000,000	[6]2,000,000	[2]	1,016,000	1,626,000	1,626,000	2,032,000	[2]	[2]
United States (sold or used by producers)	3,817,368	4,066,943	4,764,921	4,718,780	5,208,508	5,462,938	5,899,921	6,970,827	9,233,049	8,807,963	9,131,173
Total[8]	11,500,000	10,933,000	9,510,000	9,701,000	7,540,000	9,746,000	11,420,000	14,581,000	18,294,000	18,493,000	19,412,000

(¹) In addition to countries listed, Angaur Island, China, Formosa, New Caledonia, and Republic of the Philippines produce phosphate rock, but data of output are not available.

(²) Data not available.

(³) United States zone only.

(⁴) Preliminary data for Noto Peninsula, Honshu, for fiscal year ended March 31 of year following that stated.

(⁵) January to September, inclusive.

(⁶) Estimate.

(⁷) Exports.

(⁸) Totals represent only those countries for which statistics are shown.

phosphatic fertilizers. Very fine grinding, liberal application, and the presence of substantial amounts of organic matter in the soil are important factors in determining the effectiveness of raw ground phosphate rock as a fertilizer. Bartholomew[2], in studying the effect of ground phosphate rock on soils of varying acidity, concluding that the availability of the P_2O_5 decreased as the fluorine content increased. However, even when all conditions are favorable for its utilization, this product should not be expected to give as quick returns as the more soluble phosphatic fertilizers.

World's Production and Reserves of Phosphate Rock

In spite of the fact that certain phosphate fields have not yet regained their prewar positions, and accurate figures of the output from other deposits are not available, the output of phosphate is unquestionably greater today than ever before in the world's history. This increase is due in part to the need for phosphatic fertilizers to build up the soils that were depleted of plant nutrients during the war period, but mainly to the wider appreciation of phosphates for both agricultural and industrial use. As far as figures are available, the main increase in the production of phosphate rock has been in the United States and Northern Africa, but there is little doubt that the U. S. S. R. has also stepped up its output.

The world's annual production of phosphate rock for the period 1939 to 1949 inclusive, according to the figures of the U. S. Bureau of Mines[16], is given in Table 4. These figures do not include such natural phosphates as guano and bone, nor the large annual tonnages of basic slag that are obtained as a by-product of the steel industry and which relieve to some extent the drain on the world's reserves of phosphate rock.

The location of the principal known deposits of phosphate rock are shown on the map (Figure 1) compiled by Noyes[20].

The phosphate rock reserves of the world have been estimated from time to time during the past three decades[14, 19, 21, 23], and while many millions of tons have been mined and consumed in this period, the estimates as far as the United States is concerned have grown greater with the passing years[19, 23, 25].

This apparent paradox is due to three factors: (1) discoveries of new phosphate fields; (2) extensions of known deposits; (3) metallurgical developments that have brought lower grade phosphates and former plant wastes into the economic picture.

The Moroccan phosphates and the vast apatite deposits of Russia are outstanding examples of important but comparatively recent discoveries; the finding of phosphate rock in Montana is an example of the extension of well-known phosphate fields; finally, the development of flotation processes for beneficiating phosphate rock and the advent of thermal reduction
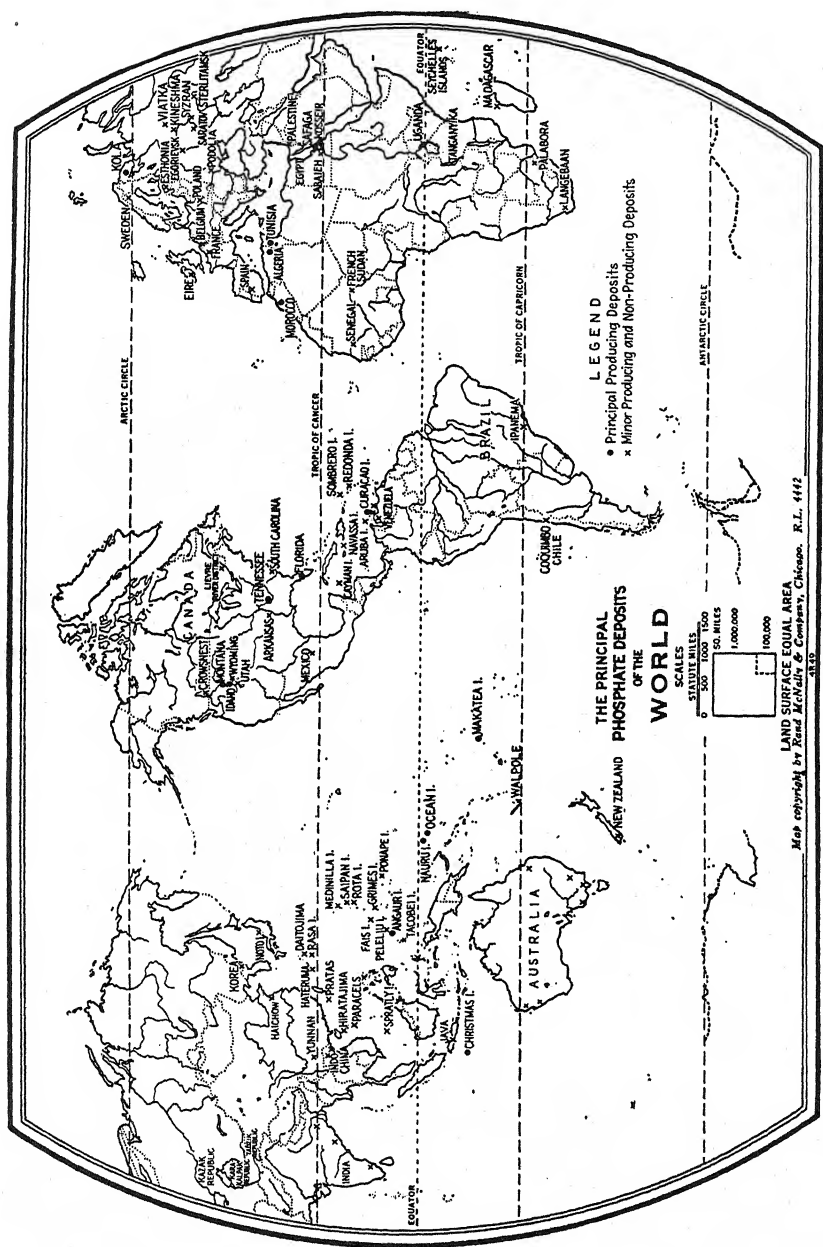
FIGURE 1. Map of the principal phosphate deposits of the world. (Deposits in the Kazak, Kara-Kalpak, and Tadzik republics in Asiatic Russia, and those of Tanganyika in Southeast Africa not identified because exact location unknown.)

methods whereby low-grade deposits can be efficiently exploited are out-standing examples of improved metallurgical practices.

Not only does phosphate rock from various sources range widely in grade but the P_2O_5 content of an individual deposit may vary considerably. Mere tonnage figures, therefore, are by no means a true measure of a nation's reserves. For instance, each ton of the high grade phosphates from

TABLE 5. ESTIMATE OF WORLD RESERVES OF PHOSPHATE ROCK AND APATITE
(*in metric tons*)

Tunisia	1,500,000,000
Algeria	1,016,500,000
Morocco	1,000,000,000
Egypt	179,000,000
Europe (excluding Russia)	435,126,000
Russia	7,568,000,000
Palestine	4,000,000
Canada	181,000
Mexico	214,500,000
Brazil	573,000,000
Ocean and Nauru Islands	282,245,000
Makatea Island	10,000,000
Christmas Island	50,000,000
Japan and mandated islands	28,984,000
China	2,400,000
Indo-China	55,000
India	10,128,000
Netherlands Indies	1,000,000
Other foreign deposits	2,496,000
Total foreign deposits	12,877,615,000
United States	13,503,514,000
Total world reserves	26,381,129,000

Sources: George R. Mansfield; K. D. Jacob; private.

certain islands in the Pacific and Indian Oceans containing an average of 36 per cent P_2O_5 is equivalent to 1.2 tons of Egyptian rock containing only about 30 per cent P_2O_5, or to 2 tons of Russian apatite, some of which may contain (before beneficiation) only 18 per cent of P_2O_5. More-over, the nature of many phosphate deposits is such that no accurate tonnage figures can be made without systematic and extensive prospecting.

The figures showing the world reserves of phosphate rock by countries compiled by Noyes[20] from the data of Mansfield[19] and Jacob[14] are given in Table 5, and the reserves by continents based on these same figures are shown graphically in Figure 2 which was drawn by Johnson[15].
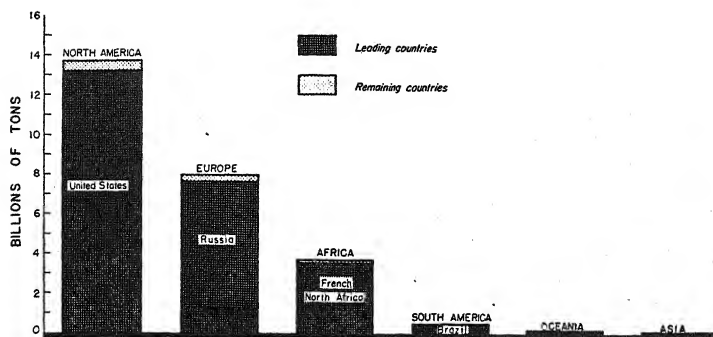
(Courtesy of U. S. Bureau of Mines.)

FIGURE 2. America's dominant phosphate position. Phosphate rock reserves of the world by countries and continents.

In some cases, the figures for individual countries are merely rough approximations and are subject to considerable change as explorations are continued.

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4. Florida Hard Rock Phosphate

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The hard rock phosphate region lies towards the west side of the Florida peninsula, extending in a north and south direction from Suwannee and Columbia Counties to Citrus and Hernando Counties, a distance of over 100 miles. Excellent transportation facilities are furnished by two railroads and most of the material is transported to ports on both sides of the peninsula and from there shipped chiefly to foreign countries.

The hard rock phosphate probably belongs to the Pliocene epoch of the Tertiary period[2], but there is some difference of opinion concerning its exact geologic age[9, 12]. The rock occurs as nodules and boulders in irregular pockets which vary in size from a few square yards to several acres in extent. These nodules are imbedded in a matrix of sand, clay and soft phosphate. The deposits, which are covered by an overburden of sand and clay, varying from a few inches to 30 feet or more in thickness, usually rest upon a thick and relatively pure light-colored cavernous limestone known locally as the Vicksburg formation.

Numerous theories have been advanced to explain the origin and formation of these deposits and since the remains of terrestrial and marine life are closely associated with phosphate the earlier geologists favored the theory that they were largely derived from organic sources[1, 3, 6].

Matson[9] states that with few exceptions the deposits are all of secondary origin. Sellards[12] believes that the hard rock deposits are derived from formations of upper Oligocene Age which are now almost entirely lacking in the phosphate area, but which are found bordering these regions. He considers that the hard rock deposits are made up largely of the residue of these formations which have disintegrated in place; that the replacement of the original limestone by calcium phosphate was an important factor in the formation of these deposits; also that the precipitation of phosphoric acid from solution contributed further to the enrichment of these deposits.

While hard rock phosphate varies considerably in its physical properties, on the whole it consists of hard white or cream-colored nodules or boulders, sometimes having cavities filled with foreign material derived from the matrix of sand and clay with soft phosphate in which the material is imbedded. The phosphate beds vary greatly in thickness (even within a

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small area), ranging all the way from a few feet to 70 feet or more. The percentage of recoverable rock in the matrix also differs widely from place to place. The average grade of rock after washing and drying is 77 per cent tricalcium phosphate (bone phosphate of lime) and less than 3 per cent iron and aluminum oxides.

Prospecting

During the early days of the Florida hard rock phosphate industry, deposits were located chiefly by outcrops and by digging shallow holes. These surface indications however were often unreliable and gave little information as to the depth and extent of the deposit. Prospectors soon learned to use the cup method which enabled them to decide whether or not the phosphate beds were sufficiently large to warrant exploitation.

The cup is a vertically slit cylinder, about 1 foot long and 3 inches in diameter, attached to drill rods or pipes in 5-foot lengths, additional lengths being screwed on as the depth of the hole increases. This method of prospecting is only applicable to depths of about 30 feet and cannot be used when the cup strikes a boulder or the deposit is below water level. When the water level is reached, 2-inch casing is lowered to the bottom of the hole and driven ahead for $2\frac{1}{2}$ feet and the core is removed by churn drilling with a jet drill bit. This sequence is repeated as long as the nature of the cores warrant it. Such equipment permits prospecting to a depth of 125 feet below the surface[5, 11].

Preliminary prospecting involves about 2 holes per acre. If the results are favorable, as indicated by the quantity and analysis of the phosphate in the matrix, additional holes are drilled, and before actual mining operations are begun, at least 16 holes per acre are sunk. The average cost of prospecting in 1944 according to Kibler[7] was from $200 to $250 per acre.

Mining

Florida hard rock phosphate is mined by first stripping the overburden of sand and clay and then digging out or dredging the phosphate stratum thus exposed. In the early days the thickness and character of the overburden was often a determining factor in the cost of production, since hand labor and scrapers drawn by mules were largely used. Now, however, the overburden is handled hydraulically and deposits which involve stripping 70 feet of overburden may be economically worked. The quantity that can be removed is governed mainly by the ratio of the overburden and matrix to the recoverable phosphate in the deposit. Kibler[7] states that an economic ratio is from 6 to 10 cubic yards of overburden per long ton of recovered rock, or 10 to 15 cubic yards of overburden and matrix combined per long ton of rock.

The type of mining used (dry or dredge) depends on whether or not the deposit occurs above or below the normal watertable. In the former case, an electric shovel is used in digging the matrix; in the latter case, a large dredge is floated in the water-filled pit and the matrix scooped up and loaded into cars which are hauled to the washer plant. In recent years a walking dragline (equipped with a 3-cubic yard scoop) has been used successfully for mining deposits as much as 45 feet below water level. Such machines can mine from 150 to 200 cubic yards of matrix per hour. Where boulders are encountered which cannot be handled either by the electric shovel or dragline, it is necessary to break them up with dynamite.

Washing and Drying

The matrix is loaded into side-dump skip cars having a capacity of about 7 cubic yards and hauled to a central plant where it is dumped on a corrigated rolling grizzly and the clay matrix loosened to some extent by a heavy stream of water. The material passing through the grizzly goes into a sump box, while the coarser material discharges into a single-roll crusher set to reduce the larger lumps to at least 7 inches. The crushed material then goes to a single-shell rotary screen having openings $1\frac{1}{4}$ inches in diameter, the undersize material passes to the sump box previously mentioned, while the oversize, after being crushed to 3 inches, pass to the log washers. The overflow from the sump box, carrying clay in suspension, is discharged to waste while the coarser material is pumped over a 10-mesh vibrating screen which separates the coarse and finer sizes; the coarse material passes to the log washers, and the finer material (-10 mesh) continues to two hydroseparators for further cleansing.

The coarsest material ($1\frac{1}{4}$ to 3 inches) after being treated in the log washers is discharged into a double-shell trommel screen where it is separates into two sizes. The larger size $(+1\frac{1}{2}$ inches) goes to a picking belt where skilled laborers remove clay balls, flint and limestone before the product receives a final crushing and goes to a storage bin.

The smaller size, retained by the outer shell of the rotary screen ($\frac{1}{16}$ x 1 inch), goes directly to storage. All the material which passes this outer screen goes to the hydroseparators for further treatment. Immense quantities of water are required in the elaborate washing and screening steps.

During the past 20 years the washing and separating equipment employed in the hard rock fields has been vastly improved with a corresponding improvement in the percentage of marketable products recovered. Deposits that would have been considered impracticable to mine in the early days are now being economically exploited and fine granular material formerly discharged into waste ponds is being saved.

The size of the phosphate rock marked ranges from $1\frac{1}{2}$ inches down
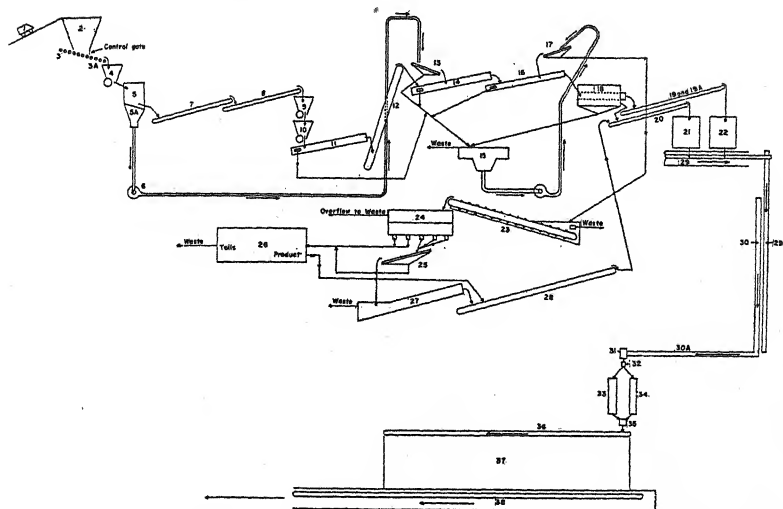
FIGURE 1. Flow sheet of Section 12 Mine, Kibler-Camp Phosphate Enterprise, Dunnellon, Florida. (August 1950)

1. Skip car from pit.
2. Hopper.
3. Rolling grizzly 6″ openings.
3a. Smooth rolls where we remove large flint and lime rock.
4. Single roll crusher 24″ × 54″, Set 6″–7″.
5. 6′ x 7′ x 14′ Screen, 1¼″ round holes.
5a. Pump sump.
6. 8″ Centrifugal pump.
7. Picking belt, Reject to waste.
8. Conveyor belt.
9. Single roll crusher, Set 4″.
10. Single roll crusher, Set 2″–2½″.
11. Duplex log washers 30′ long.
12. Chain elevator.
13. Vibrating screen, 10 mesh.
14. Duplex log washer 30′ long.
15. 20′ Dorr hydroseparator.
16. Duplex log washer, 30′ long.
17. Vibrating screen, 8 mesh.
18. Double shell rotary screen, ⅜″ x 1″ inside, $\frac{1}{16}$″ x 1″ outside.
19. Picking belt.
19a. Conveyor belt.
20. Conveyor belt.
21. Steel receiving bin.
22. Steel receiving bin.
23. Dewatering drag.
24. 2-Dorr sizers in parallel, 5 pockets each.
25. Vibrating screen, 16 mesh.
26. 4 Tables in parallel.
27. Dorr rake classifier.
28. Belt conveyor.
29. Tunnel and belt conveyor.
29a. Inclined belt conveyor to wet storage.
30. Recovery tunnel and belt conveyor under wet storage.
31. Receiving bin.
32. Chain elevator.
33. Rotary dryer.
34. Rotary dryer.
35. Chain elevator.
36. Conveyor to dry storage.
37. Dry storage shed.
38. Tunnel and belt conveyor under dry storage for loading into railroad cars.

Between elevator (32) and dryers (33) and (34) there are two vibrating screens and two crushers, so arranged that we can make two maximum sizes to suit customer's specifications.

to +35 mesh and the grade from 72 to 82 per cent BPL. Virtually any grade between these two extremes can be obtained by blending the different sizes that are separated at various stages of the washing process.

A flow sheet of a modern hard rock washing plant is shown in Figure 1.

For many years washed Florida phosphate was dried by piling up alternate layers of rock and wood then firing the latter. This crude method was abandoned when timber became scarce and the rock is now dried in oil-fired rotary kilns.

Until recently, the wet rock was shipped from the mines by rail to the port of Fernandina, Florida, where it was dried, stored and the bulk of it exported. The drying, storing and shipping facilities at this port took

TABLE 1. ESTIMATED RESERVES OF PHOSPHATE ROCK IN MAIN HARD-ROCK FIELD

Reserves	Acres	Long Tons	
		65% BPL	40–65% BPL
Known	4,032	41,280,840	10,702,440
Probable	69,308	580,107,960	150,398,360
Total known and probable	74,240	621,388,800	161,000,800
Possible			
Area examined by Aikin		417,971,200	107,400,500
Additional area	46,000		230,000,000
Combined total	120,240	1,039,360,000	498,501,300

care of the entire production from the hard rock field, but the reduced output in recent years did not warrant maintaining this expensive plant and it has been closed down. Drying operations are now performed at the mines and all dried rock for export is shipped from Port Tampa, Florida.

There is still a limited domestic demand, however, for this high grade rock. Although the average grade of Florida hard rock phosphate is appreciably higher than Florida pebble phosphate, the deposits of the latter are more regular and extensive, and as a result can be mined more economically. The higher mining cost of hard rock phosphate however is offset to some extent by the premium paid for this higher grade product.

Kibler[7] states that over a period of many years the yield of hard rock has averaged about 14,000 tons per acre. Undoubtedly this yield would have been considerably higher had more efficient mining and processing equipment been developed before so many deposits were presumably exhausted and abandoned.

Production and Reserves

During the period 1888 to 1939, 75 companies were engaged from time to time in mining hard rock phosphate, but only one concern (Kibler-Camp Phosphate Enterprise) is now actively exploiting these deposits.

Although the production of Florida hard rock phosphate has fallen off considerably because of competition offered by the more extensive and cheaply mined pebble deposits, the former fields are by no means exhausted.

Mansfield[8] estimated the total reserves of hard rock phosphate of grades ranging from 45 to 65 per cent BPL at more than a billion and one-half long tons, as shown in Table 1.

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5. Florida Pebble Phosphate

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INTRODUCTION

A study of the geology of Florida pebble phosphate deposits indicates a large area. Active mining, however, is carried out in an area approximately 15 by 30 miles, beginning at one end of Plant City and continuing to a point somewhat below Ft. Meade. Active mining is confined to this region because of the grade of pebble deposits and the concentration of values. Phosphate pebble can be found throughout this particular area at an economic depth and in considerable quantity.

The grade of the concentrated product fixes its saleability. At the present time, there is little sale for rock under 65 per cent BPL, the most desirable grades ranging from 72 to 77 per cent BPL.

At present there are seven companies actively engaged in mining in this area. They are American Agricultural Chemical Company, American Cyanamid and Chemical Corporation, Coronet Phosphate Company, Davison Chemical Corporation, International Minerals and Chemical Corporation, Swift and Company, and Virginia-Carolina Chemical Corporation. The 1948 production of these companies totaled a little over 7,000,000 tons of product. The largest company produces currently nearly three million tons and the smallest about 400,000 tons yearly. This tonnage is divided between coarse pebble +1 mm in size and flotation concentrates −1 mm to 200 mesh. The bulk of the tonnage coming out of Florida at the present time is from concentrates.

Location of the Deposits

The so-called pebble phosphate is known to exist in scattered localities from Polk County northward into Georgia. At present, all of the commercial rock, however, lies in a roughly circular area about 30 miles in diameter, mostly within Polk and Hillsborough Counties, as shown on the accompanying map (Figure 1).

Physical Features

The land surface of the area is flat pine upland with an elevation of from 100 to 150 feet. The eastern edge of the area is drained by the Peace River,

heading close to Lakeland and flowing almost due south to the Gulf of Mexico via Charlotte Harbor Bay. The central and western part is drained by both the Alafia and the Myakka Rivers and their tributaries the Myakka flows southwestward into Charlotte Harbor Bay; the Alafia flows westerly into Tampa Bay.
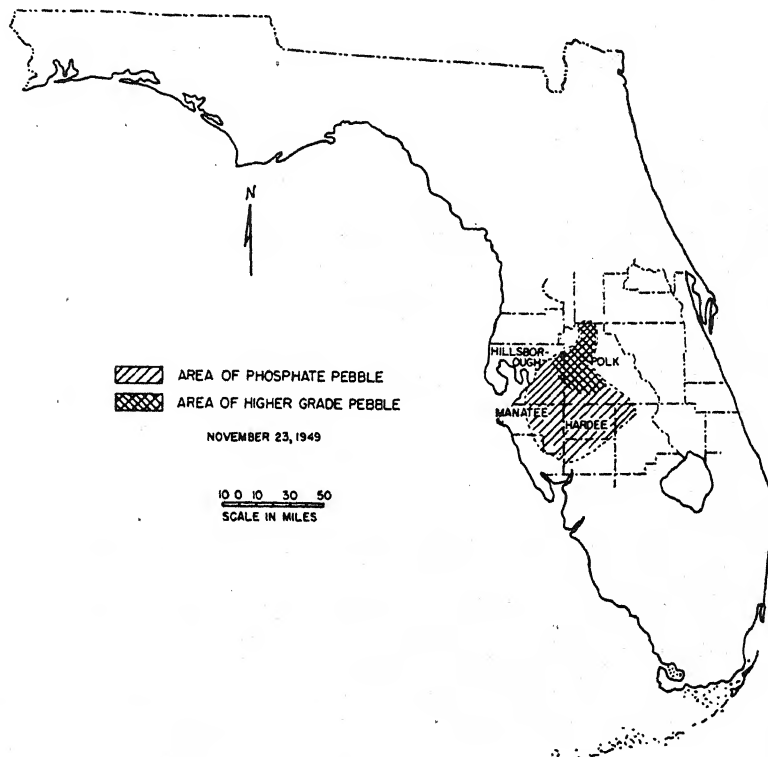
FIGURE 1. Outline map of Florida showing pebble phosphate area.

The rock underlying the area is nearly horizontal. The oldest bed exposed is part of the Hawthorn phosphatic limestone of Miocene Age. This outcrops in the stream beds of the Peace and Alafia Rivers. The Hawthorn is covered elsewhere except where it has been exposed by mining operations.

The Bone Valley formation of Pliocene Age, which is the phosphatic stratum extensively mined in this area, unconformably overlies the Hawthorn. Resting unconformably upon the Bone Valley formation are Pleistocene terrace deposits of unconsolidated quartz sand which comprise the overburden of the phosphate ore.

Distribution and Character

The economic deposits all lie within the Bone Valley formation and include those which, with the silicates and fines removed, will analyze above the 65 per cent tricalcium fluophosphate or bone phosphate of lime (BPL).

The phosphate itself is found as rounded pellets ranging from −350 mesh and smaller to some over a foot in diameter. The bulk of the pellets lies within a range of −150 to −1 mesh, the size distribution varying markedly from one field to another. The particles are commonly highly polished but may be dull in luster.

The deposits are fairly continuous over large areas in grade (of concentrated pellets) and thickness, but locally both may change abruptly. The thicker and higher grade deposits lie in the northern part of the area as shown on the map (Figure 1).

Mining

General

The area included in these mining operations is quite flat and lies at an elevation of 100 to 150 feet above sea level. The deposits occur with an average of 15 to 20 feet of overburden which may contain some phosphatic values (too low in P_2O_5 content to process), and from 10 to 30 feet of material designated in the field as matrix. Matrix is made up of three constituents: (1) clay slimes, largely −5 microns in size; (2) silica sand, largely − 1 mm; and (3) phosphate pebble, ranging in size from a small quantity at $1\frac{1}{2}$ to 2 inches down to 400 mesh. The screen size distribution of the pebble will vary considerably from one location to another.

Prospecting

While deposits are fairly uniform, it is necessary to carefully prospect areas to be mined to determine the depth of overburden, matrix, yield of product per acre, and the grade of product to be produced.

If the prospecting survey of the piece of land is exploratory, 4 holes will be put down to every 40 acres, usually diagonally across the acres, to determine the general nature of the deposit. Most mining and calculation of reserves is based on 16 holes to 40 acres. In special areas, holes may be put down rather closely spaced to determine the exact nature of the deposit.

The method of obtaining the prospect sample or core varies to some degree with the company taking the sample. Machine coring is to a large extent supplanting hand augering at the present time. In the case of hand augering, the equipment used for prospecting is relatively simple. A casing having an inside diameter of $4\frac{1}{2}$ inches is forced into the ground by means of the weight of the pipe, pressure of the crew on the pipe, and the cutting

action of hardened teeth on the lower edge of the casing. As the casing bores into the ground, a hand auger is placed inside the casing to remove the material displaced.

In general, the casing is in 5-foot threaded sections. The auger is a standard unit fastened to a $\frac{3}{4}$-inch iron pipe to which additional 5-foot sections
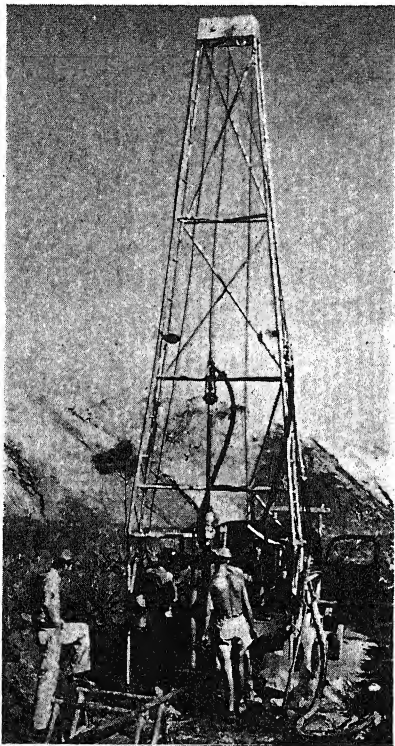
(Courtesy of Int. Minerals & Chem. Corp.)

FIGURE 2. Drilling rig used in prospecting for Florida pebble phosphate.

are added as the depth of the hole increases. In driving one core to a depth of 80 feet, it may take a crew a day to put down a single drill hole.

The high cost of labor often makes the use of machine coring rigs more economical than hand augering. Figure 2 shows one of these outfits drilling holes in a pebble field. In general, no casing is used with these drills. The cores obtained are for the most part disturbed cores and do not represent the true structure of the beds as deposited. No completely satisfactory method of coring the deposits has been found as yet, but the methods in use check very closely with mining recovery.

The cored material is sent from the field into the laboratory where it is processed in a manner similar to plant processing. The data recorded will give the depth of overburden, depth of matrix, grade of pebble, grade of concentrate, cubic yards of matrix to be mined per acre and tonnages of products per acre. The value of the land can be determined from this data, as well as the advisability and economics of mining the property.

Mining Operation

In the first land pebble phosphate mining operations in Florida, over-burden was removed by steam shovels, hauled in tram cars, and deposited on unmineable land. The matrix was then mined and sent to the plant. The next development was the removal of overburden by the use of hydraulic guns. The overburden was then pumped into mined-out areas or to a debris dump. The matrix was hydraulically mined and pumped to the plant.

At present the overburden is removed by draglines and dumped into the previously mined-out cut. This operation is much more economical and gives better recovery of mineable values. At most operations, the matrix is mined by a dragline and dropped into a shallow pit on the surface of the ground from where it is pumped to the plant.

A dragline operation starting in a new pit will first make a box cut at the edge of the property. The overburden is removed and piled on the ground on top of the overburden that will be removed in the second cut. If the new operation is next to an old mined-out pit, this, of course, is unnecessary. The overburden from the first cut has to be rehandled, but the values in the rock beneath this first cut warrant such rehandling. The length of cuts taken by the dragline will depend upon the shape of the property. However, they are seldom less than a quarter of a mile in length and often run for a mile. The width of the cut depends on the dragline used. A cut as wide as feasible for the boom length and depth of the deposit involved will be made. If the mining operation is carried out with two drag-lines at the same location, one may remove overburden while the other removes matrix.

Figure 3 shows an operation involving a Bucyrus 1150B walking Monighan. This dragline has a bucket capacity of 23 cubic yards and a 215-foot boom. It is easy to see the line of division between overburden and matrix in this picture. The top section or overburden is removed and cast away from the unmined area, as indicated by the spoil piles in the background. The matrix is then mined and dropped in what is called a well, which is an area dug out of the surface of the overburden. The suction end of a large sand pump is then dropped into the well and the mined matrix washed into the suction of the pump by means of hydraulic guns.

Figure 4 shows the hydraulic operation at the well. The hydraulic pressure from the gun breaks down the mud in the matrix and washes the matrix

(Courtesy of Int. Minerals & Chem. Corp.)

FIGURE 3. Aerial view of mining operations in the Florida pebble phosphate fields.
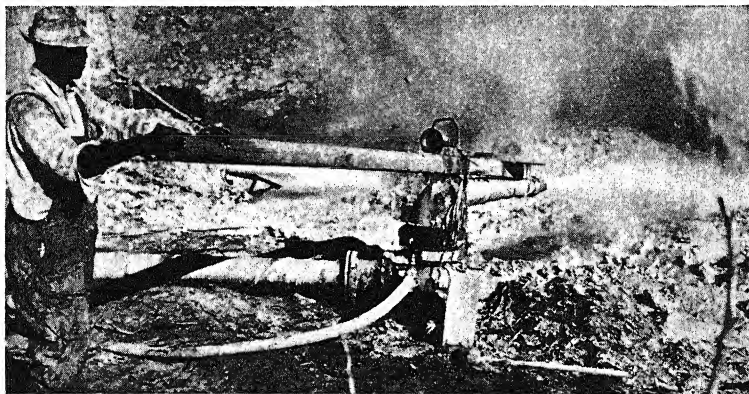
(Courtesy of Int. Minerals & Chem. Corp.)

FIGURE 4. Hydraulic gun used to wash the matrix containing pebble phosphate into a sump from which it is pumped to the washer plant.

to the pump suction. From this point it is pumped to the plant. The entire operation is electrical. Power lines are run to the dragline and to the well. The whole mining unit is mobile. The pump which pumps the matrix to

the concentration plant and the motor which runs it, together with the necessary electrical switches, are all assembled in a sled, the entire unit being described as a pit car. The pit car can be hauled by tractor to the next location and the necessary pipe lines and electrical connections made.

For average-size draglines, the pit car, which handles the matrix to the concentration plant, is equipped with a 300- to 500-h-p motor. A sand pump operating at 600 to 720 rpm pumps from the pit to the washer up to 600 cubic yards per hour with about 6,000 gallons of water per minute. Where large draglines are used with larger pumps and motor, quantities up to 1,000 cubic yards per hour have been pumped. The pipe line from the pit car to the concentration plant is 14 to 16 inches in diameter. It is not unusual to pump a distance of 1 to 2 miles in the Florida area. However, additional booster pumps must be put in the line to maintain proper velocity for pumping. In order to prevent all possible choke-downs in the pipe, a velocity of 10 to 14 feet per second should be maintained in the pipeline.

The hydraulic guns at the pit car which furnish the water for pumping help to break down the matrix for further treatment. The minimum pressure at these guns is 100 psi, and where a mud of an unusually sticky nature is found in the matrix, this pressure may be stepped up to 200 to 225 pounds. This hydraulic action prepares the matrix for further processing.

There is quite a problem in disposing of the clay slimes in the matrix after washing. Mining is so designed that the area after mining can be used to settle out these clay slimes, and careful consideration must be given to this when laying out the mining operation.

Mining Auxiliaries

The following list represents a number of the auxiliary operations handled by the mining operators.

(1) Clearing land for mining.
(2) Dragline operations.
(3) Transportation of water to the mining operation and pumping matrix from the operation to the concentration plant.
(4) Establishment of power lines to and from the mining operation.
(5) Operation of a settling area for slime in the matrix.
(6) Operation of tailings dams for handling concentration tails.
(7) Operation of excavators for ditching and dam construction.

The amount of land that is is necessary to clear before mining depends upon the characteristics of the dragline which is to be used. All timber is removed and salvaged where possible. Bulldozers then move in and scrape the surface, putting most of the roots, stumps, and brush into piles where they are burned. With a walking dragline of considerable size, it is often

cheaper to level the area with a bulldozer than with a dragline. Often a bulldozer and dragline will work together on the levelling operation.

An electrical crew handles the power to and from the dragline. In mining a considerable area, a temporary sub-station is set up. Temporary lines are then run from the sub-station to transformers constructed on skids. A long-flexible cable along the ground delivers the power from this mobile sub-station to the dragline. Temporary power lines also run to the pit car and to pumps in the pit to keep the bottom of the pit dry during mining operations. If the bottom of the pit is not kept dry, there will be considerable loss in the recovery of the phosphate matrix.

Additional settling areas are constructed over and above the area of the mined-out pit for settling out the clay slimes in the matrix and for the recovery of water for re-use. These dams are constructed and maintained by the mining department. At the new Noralyn operation of International Minerals and Chemical Corporation, one such area covers about 480 acres. Operation of this area includes maintenance of the dams and operation of spillways to insure clear water overflows.

The silica tailings from the concentration plant are disposed of in dammed-up areas, usually in mined-out pits. The silica tailings are piped from the concentration plant to the point of disposal. Water from this area is recovered for re-use in most cases.

Each operation has a considerable number of small excavators, both draglines and shovels, for ditching and dam building. These excavators, together with miscellaneous tractors, maintain the operation as a whole.

CONCENTRATION

General

Early operations in Florida involved a simple washing and screening operation. The matrix was sent to a washer which consisted of screens and log washers. When the matrix had been disintegrated, the slimes washed out, and the granular material screened on 1 mm, it was found that the +1 mm was a saleable grade of phosphate rock. Deposits in the area produced this coarse pebble rock having BPL values up to 80 per cent with large areas above 72 per cent BPL.

The fine granular material which passed through 1 mm screens contained a large proportion- of the phosphatic values mined. Because of the silica present, however, its grade was low and there was no known method for concentration. The fines were dumped with the slimes and overburden in mined-out areas. Although phosphatic values in the ground were wasted with this process, the operations were economical.

In the early 1920's, experimental work was started to develop a flota-

tion process for the concentration of the granular fines (-1 mm) then being discarded in the field. The first pilot plant was built in 1927 and erected in connection with what is now one of the plants of International Minerals and Chemical Corporation. The process employed patents developed by Broadbridge and Edser in 1925, in which a froth flotation process separated the fine phosphate pebbles from the silica sand impurity. Trotter and Wilkinson developed this fatty-acid float to a practical point for use in flotation cells. This process did not work well on material -1 mm $+28$ mesh, and in 1929 Chapman and Littleford applied for a patent, issued in 1934, covering the agglomerate tabling of this coarser fraction.

At present there are three processes used in concentrating matrix, namely: (1) washing and screening the $+1$ mm; (2) agglomerate flotation of the -1 mm $+28$ mesh material; (3) cell flotation of the -28 mesh $+200$ mesh.

The screen size distribution of the phosphatic values in the matrix varies considerably from one area to another. Some areas have practically no phosphatic values in the -1 mm, thus, a simple washing operation is justified on such rock. In other areas there will be considerable phosphatic values in the -1 mm $+28$ mesh but practically none in the -28 mesh fraction and here a washing plus an agglomerate flotation operation on the -1 mm $+28$ mesh are justified. Where the values extend down into the extreme fines, the three operations are combined.

Washing

The washing operation starts when the matrix is delivered from the pipeline transporting it from the mine. This pulp contains some mud balls and lime rock up to 8 inches in diameter. It is necessary for the coarse mud balls and the lime rock to be disintegrated before further processing. It is usual to discharge the matrix into a screen tub launder with a 1-mm slotted flat screen in the bottom. A large proportion of the slimes, fines, and water will immediately pass through this screen. The coarser material is delivered to a trommel which removes everything $+2$ inches. At the present time, it is fairly general practice in the field to break down this oversize material by the use of hammermills. The reduced product is then returned to the head of the washer. All of the washer reject will pass through the 1-mm flat screens.

There is a considerable amount of mud balls mixed in with the coarse phosphate pebble and these must be broken down and washed out. Log washers in series are used for this process. One log washer discharge often goes to a second log washer in series. A typical washer flow sheet is shown in Figure 5. This is the flow sheet of the Varn washer of Swift and Company.

Most washers deliver two wet products to final shipping bins: (1) a $-\frac{3}{4}$ inch, $+\frac{3}{8}$ inch and (2) a $-\frac{3}{8}$ inch $+$ 1 mm. In general, the finer pebble product is of considerably higher grade.

Concentration of Fines, General

The discharge through the 1-mm screens from the washer, called the washer debris, contains all the clay slimes in the matrix, the silica sand,

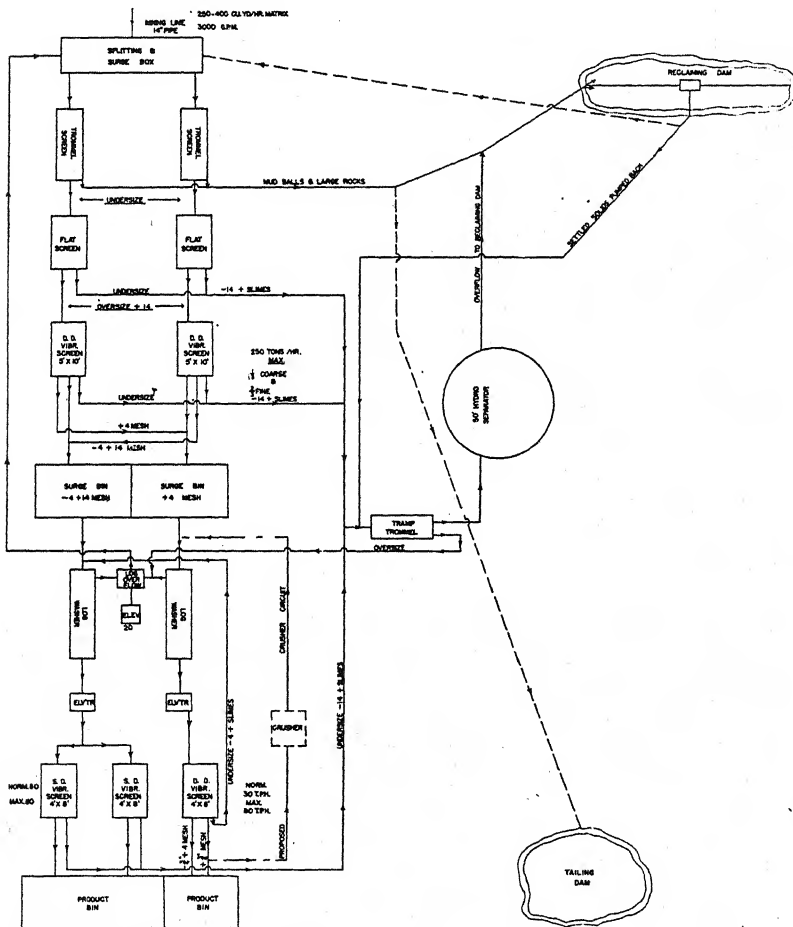FIGURE 5. A typical washer flow sheet in the Florida pebble phosphate fields.

−1 mm, and the phosphate pebbles, −1 mm. For further concentration, it is necessary to remove the slimes since they have a very adverse effect on flotation reagents. These particles are very fine, have a large surface and tend to absorb the reagent, making reagent cost prohibitive.

The slimes contain phosphatic values and run between 20 and 30 per

cent BPL. The phosphatic values are present as finely divided collophane, (this is the name of the mineral making up the phosphatic pebble), iron phosphate, and aluminum phosphate. Also present are very finely divided silica and numerous decomposition products from feldspars and clay minerals. No economic method of concentrating the phosphatic values in the slimes has, as yet, been proposed. A fairly large proportion of the phosphate in the matrix is discarded in this slime fraction. It is quite usual for the slimes to contain 25 per cent or more of the values. Research programs are being carried out at the present time for handling these slimes.

The processing of the washer debris consists of the removal of the slimes. This is usually done in the field in one of three ways:

(1) The washer debris is sent to a large diameter hydroseparator where the slimes, −200 mesh, overflow or,

(2) The fines are sent to a small diameter tank or hydroseparator, where the coarser fraction of the fines is removed, and the overflow of the small hydroseparator or tank, containing a reduced tonnage, is sent to a large diameter hydroseparator for recovery of all values +200 mesh.

(3) The washer debris is sent to a multiple unit cone classifier which separates the −200 mesh slimes from the values and discharges the values at high percent solids.

One operation does not use a large diameter hydroseparator for recovery of the finer fraction but sends this material to recovery pits where these values are caught and ultimately mined.

No matter which method is used, the settled portion still contains a considerable quantity of slimes. As many stages of further desliming as are necessary to produce a proper flotation feed follow. Most of these desliming processes consist of dewatering, repulping with additional clean water, and mixing, followed by subsequent dewatering. Dorr rake classifiers and Akins screw classifiers are standard types of dewatering and desliming equipment. Hydroseparators are used where large quantities of material are to be dewatered. The desliming operation is responsible for the major portion of the large gallonage of water used in the phosphate concentrating operations.

The size of the primary desliming hydroseparator varies with the size of the phosphate particles to be recovered. A small hydroseparator or v-box tank is used if +48 or +28 mesh is to be recovered. The fine granular fraction is then discarded to the mud pond with the slimes.

It is necessary to have between 1 and 2 acres of mined-out pit or settling area for every acre of matrix mined. The exact amount depends considerably upon the quantity of slime present and the settling characteristics of the slime.

Sizing

When primary desliming is completed, it is necessary to size the product at approximately 28 mesh to get adequate recovery. The coarser fraction is sent for agglomerate processing while the fine fraction is sent to the flotation cells. The most general method of sizing is by use of Fahrenwald upward-current classifiers. These classifiers are usually preceded by a primary removal of fines by straight water classification. This is accom-
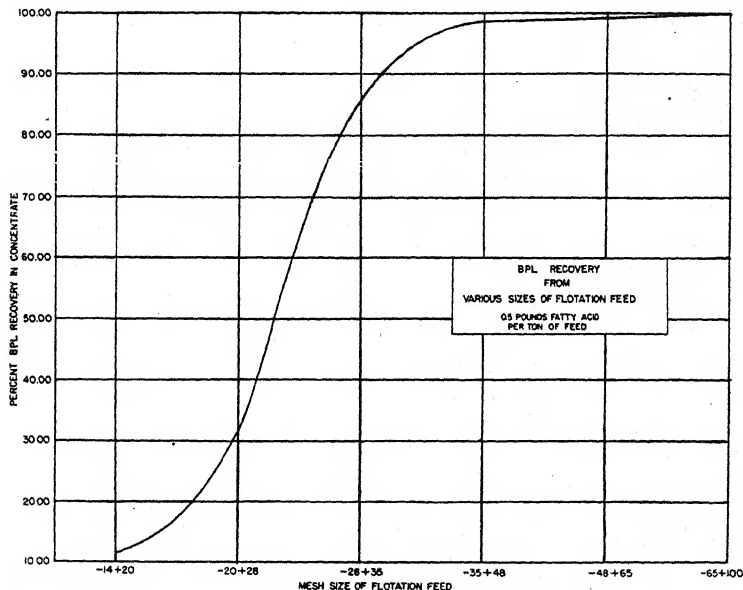
FIGURE 6. Recovery of phosphate from various sizes of flotation feed.

plished either by a small diameter hydroseparator or through rake or screw classifiers.

There is a considerable and varying amount of white, chalky phosphate which is fairly porous and has an apparent specific gravity considerably lighter than the rest of the material. This fraction will tend to flow over the Fahrenwald sizer, thus giving a bad sizing effect. Water classification on this type of material will not give proper sizing. Screens are used in some operations for sizing. They displaced the Fahrenwald sizer at the Noralyn plant of International Minerals and Chemical Corporation.

Proper sizing is quite essential to good recovery in both the agglomerate operation and the froth flotation process. Figure 6 shows the recovery of values in a flotation cell plotted against the screen size of the particles.

It can be easily seen that $+28$ mesh will be lost in the tails in this operation. Similarly, it is difficult to recover fines adequately when using the agglomerate process on the coarse material.

Concentration of the Coarse Fraction

There are several methods for treating the -1 mm $+$ 28 mesh fraction. Three of these processes involve an agglomerate float, while the other depends upon developing a gravity and friction difference in a Humphrey spiral. These processes are as follows:

(1) Agglomerate tabling (as originally used by Phosphate Recovery Corporation).

(2) Underwater screening (as originally used by Swift and Company).

(3) Spray belts (as originally used by Coronet Phosphate Company).

(4) Gravity separation of reagentized feed in a Humphrey spiral (as originally used by International Minerals and Chemical Corporation).

In all of these processes, the feed is dewatered to 60 to 75 per cent solids. The feed is then conditioned with reagents at high per cent solids, followed by separation.

The reagents used are caustic soda (the pH of this operation is held at about 9), fatty acid, kerosene, and approximately a 22°Bé fuel oil. It has been found economical to use tall oil, produced by the wood, paper and pulp industry, as the cource of fatty acid. This material as delivered will run 45 to 55 per cent free fatty acid, with another 35 per cent content of rosin acids. The tall oil is delivered in tank car lots. It is an extremely viscous material, and a light fuel oil is added as it is removed from the tank car in order to decrease the viscosity so the material can be pumped. Both the tall oil and the heavy fuel oil are kept warm (approximately 140°F) to aid in pumping through the plant for reagent addition.

The caustic is added as a solution. The strength of this solution depends upon the quantity being used and the desire of the particular operators. Caustic is bought in drums or as liquid caustic in tank cars and mixed to the desired solution strength. On a basis of pounds of reagent per ton of feed, the following approximate amounts are in general use: caustic, 0.4 to 0.8 pounds; kerosene, 1 to 3 pounds; fuel oil, 0.5 to 2 pounds; and fatty acid, 0.75 to 1.5 pounds.

The addition of reagents must be made to a high per cent of solids feed. If the reagents are added to a low per cent solids pulp, the oils simply float on top of the pulp without being adequately mixed. Figure 7 shows the per cent solids in the feed at the time of reagentizing vs. per cent recovery of the phosphatic values. From this, it becomes obvious that about 65 per cent solids are necessary for good operation.

There are in general two types of mixing conditioners used. One is the

standard vertical mixing tank with a cruciform impeller. These tanks are in series to prevent short-circuiting and to give adequate time of mixing. The other is a horizontal rotary drum with flights for lifting the feed similar to those used in a drier. This will rotate at a rather slow rate of speed, mixing the pulp and the reagents. It is a general practice to use the rotary drum mixer for the coarser feeds and the vertical type with impeller on the flotation cell feed. The coarseness of the agglomerate feed.

% SOLIDS IN CONDITIONER

VS.

%RECOVERY IN ROUGHER FLOAT

1 MIN. CONDITIONING

% SOLIDS
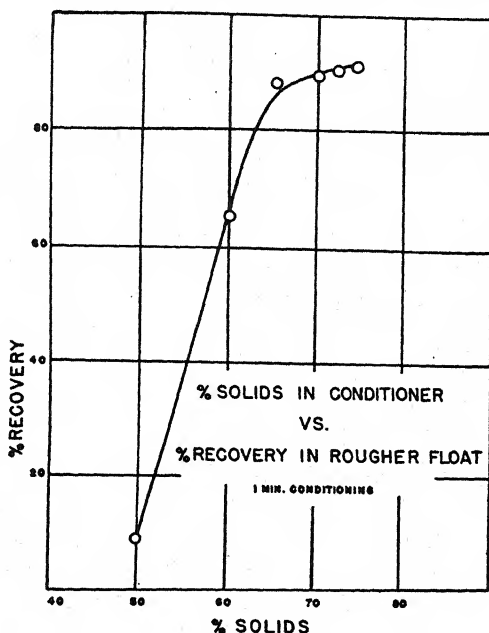
FIGURE 7.

requires high-speed impeller operation, which results in considerable power consumption. Mechanically, the drum mixer works better on the coarse feed.

Figure 8 shows the agglomerate tabling floor at one of Davison Chemical Corporation's plants. In this process, the high per cent solids reagentized feed is delivered to a distributor at a constant rate and diluted to about 35 per cent solids. This is run to a standard shaking riffled table. The reagentized phosphate particles form agglomerate flocs and make a skin float across the surface of the table. The silica sand particles drop to the face of the table and are delivered as a tailing product to the end of the table. The silica is thus delivered at the point where on a gravity separation

the high gravity material would discharge. It is usual to have a concentrate a middling product, and a tail from each table. The middling product is then circulated in the system.

In the underwater screening system used by Swift and Company, the reagentized feed is brought in above a stationary slanting 14-mesh screen which is underwater. The agglomerate phosphate flocs are too large to pass through the screen, while the silica particles, which are not agglom-

(*Courtesy of Davison Chemical Corporation*)
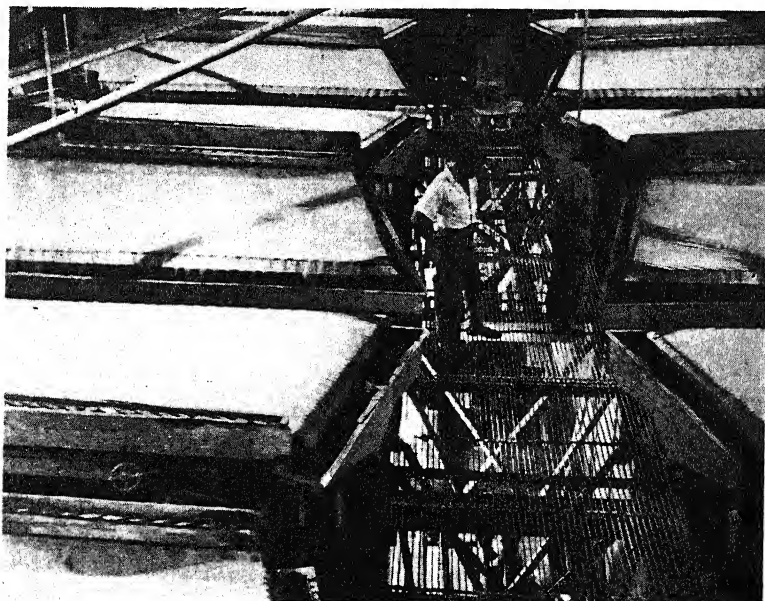
FIGURE 8. Agglomerate tabling of pebble phosphate; interior view of plant of the Davison Chemical Corporation.

erated, pass through the screen to the tailings draw spigot. At one of the Coronet Phosphate Company's plants the reagentized feed at high per cent solids is dropped on a flat traveling conveyor belt. Sprays aerate the material on the belt and wash the flocculated phosphate values over the sides of the belt, where they are collected as a concentrate. The silica sand remains on the belt and passes through as a tailings product.

Figure 9 shows a spiral installation at the Noralyn plant of International Minerals and Chemical Corporation. In this process, only enough reagent is added to change the apparent specific gravity of the phosphate particles slightly and alter the friction characteristics of the phosphate as compared

to the silica particles. In passing down through the spiral, the silica particles of higher apparent specific gravity and greater friction will be slowed down by the spiral surface and delivered to the tailings port. The phosphate concentrate is delivered as the spiral discharge.

In all of these processes, various complex flow sheets for rehandling certain products may be developed, depending upon the desire of the operating company.
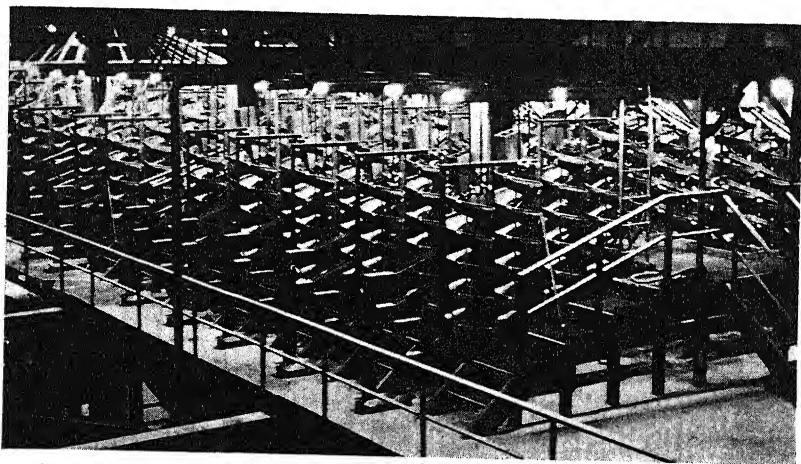
(Courtesy of Int. Minerals & Chem. Corp.)

FIGURE 9. A battery of spiral concentrators employed in recovering pebble phosphate.

Flotation Cell Concentration

Treatment of the −28 mesh fraction is pretty well standardized in the phosphate field. This fraction must be conditioned with reagents at high per cent solids just as the coarser fraction. Proper desliming is essential to low reagent cost and high recovery. In general, the cell feed is reagentized with 0.3 to 0.6 pounds per ton of caustic soda (the pH of the operation is held at about 8.6), 4 to 5 pounds per ton of 22°Bé fuel oil, and 0.4 to 1.25 pounds per ton of fatty acid. Kerosene is also used in some operations to a minor degree. The reagentized fines are diluted to about 30 to 35 per cent solids and floated in standard cells. The rougher float is usually carried out in a four-unit cell bank, since the time for phosphate flotation is quite short.

It is difficult to obtain a high grade concentrate and good recovery in the same operation. If good recovery is obtained, the concentrate is fairly low grade. The low-grade concentrate is then cleaned in cleaner cells which may be of a four or six unit cell bank. With a straight fatty acid float, it

is unusual to get less than a 5 to 7 per cent silica in the final concentrate and make good recoveries.

In 1942 Arthur Crago developed a double flotation process in which the fatty acid concentrate was subjected to treatment with sulfuric acid to remove oils and fatty acid. After this treatment, the concentrate was washed and subjected to a flotation process using amine as a reagent. In this operation, silica was floated away from the phosphate leaving a high grade
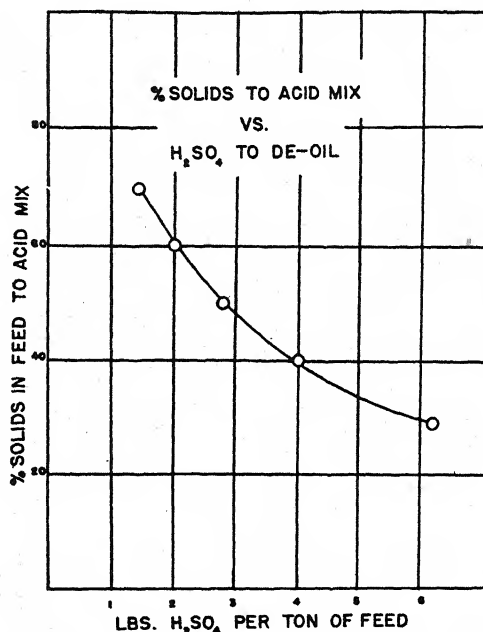
FIGURE 10. Effect of per cent solids in the acid mixture on the consumption of sulfuric acid required for efficient removal of fatty acid reagents.

concentrate. This double float has become the accepted method in the field for producing concentrates of highest practical grade.

To get ultimate recovery and highest grade, the double float is essential. An improvement can be made on the recovery by the use of stage addition of reagents in the rougher operation. Inasmuch as the reagents have to be added through conditioning at high per cent solids, it is necessary to de-water the rougher tails before reagentizing and re-treating.

Figure 10 shows the effect of per cent solids in the acid mixture on the sulfuric acid consumption for efficient dewatering. It is quite obvious that high per cent solids give optimum results.

After acid has been mixed with pulp, it is necessary to wash out both the acid and the oily water from contact with the solids to minimum amine requirements and optimum grade in the amine float.

It is not necessary to condition the phosphate rock in the amine float. Carefully washed and dewatered feed is dropped into a six-unit cell amine flotation circuit with fresh water. The float is maintained at about 30 per cent solids. The reagents for this float are added to the first cell and the silica is removed in the six-cell bank. The optimum pH for this operation is approximately 7.8. Thus, it is necessary to add enough caustic to hold this concentration.

The amount of amine consumed per ton of original feed will vary considerably with the amount of slime in the feed. Some silica has a fresh surface readily floated, while in other areas such flotation is more difficult. In general, the amount used will vary from 0.15 to 0.5 of a pound of amine per ton of final concentrate produced.

The amine reagent is added as a water solution. The strength of this solution will depend upon the tonnage being treated and the desires of the operators. The solution is kept hot, otherwise the amine will drop out of solution and coat the pipe through which it is transported.

The screen analysis of the silica in the feed to the amine section will also materially affect the reagent consumption. Figure 11 shows the reagent consumption vs. the screen analysis of the silica in the feed. It is uneconomical to float the coarser fractions in a flotation cell.

The final concentrate is dewatered and placed in shipping bins. From the shipping bins, it is loaded into railroad cars or conveyor belts and sent to wet storage facilities.

Figure 12 is an aerial view of the Noralyn plant, which is capable of putting out a million and a half tons a year of high-grade product.

<div align="center">DRYING</div>

General

From 85 to 90 per cent of all phosphate shipments from the Florida field are used in the fertilizer industry. Such shipments must eventually be ground and acidulated for either superphosphate or triple superphosphate or be finely ground for direct application to the soil. Some shipments of wet phosphate are made for use as furnace burden in the electric furnace production of phosphorus. The superphosphate plants throughout the country are in general equipped with grinding facilities for handling dried phosphate for the production of superphosphate. The phosphate industry must therefore ship a dried product to such plants.

After the pebble or concentrate has been produced, it is shipped to wet storage before drying. It is customary to keep considerable quantities of

wet phosphate on hand as a buffer between production and shipping. There is some storage of dried rock, but this is insignificant compared to wet-rock storage facilities. Figure 13 shows a wet-rock storage with trestle facilities. The phosphate is stored along the trestle according to grades and is recovered by a conveyor belt in a tunnel underneath the trestle. Rock of desired grade is drawn from the pile, deposited on the belt, and elevated to the proper feed bin ahead of the drier.
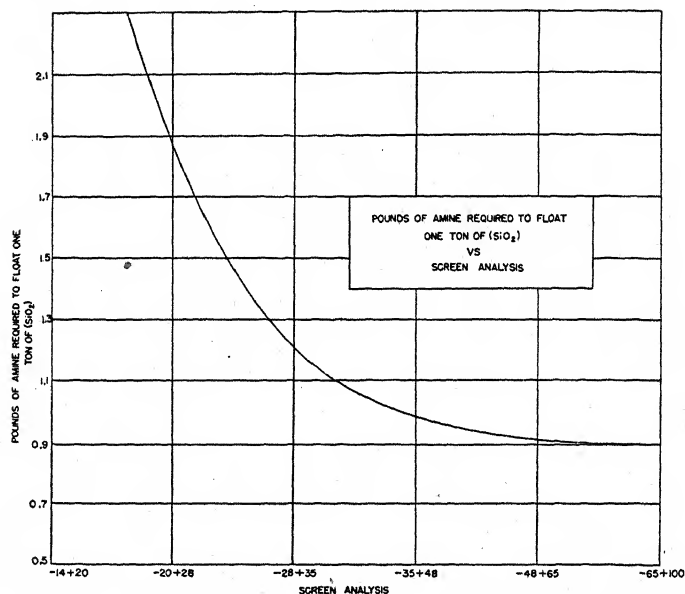
FIGURE 11. Reagent consumption vs. screen analysis of silica in the feed in the flotation of silica.

Drying Operations

Just as there has been a gradual change in the industry in mining and concentrating equipment, there has been also a change in the type of drying equipment. In recent years drying has been done entirely with rotary kiln driers. When these were first introduced in the phosphate field, the practice was to have a battery of small driers to handle 10 to 12 tons an hour. One plant had 12 such driers to handle 100 to 120 tons an hour.

Today the trend is toward installation of one large dryer to handle the same tonnage. American Agricultural Chemical Corporation recently installed a large drier as have American Cyanamid and Chemical Corporation and Swift and Company. Figure 14 shows an installation at the Noralyn
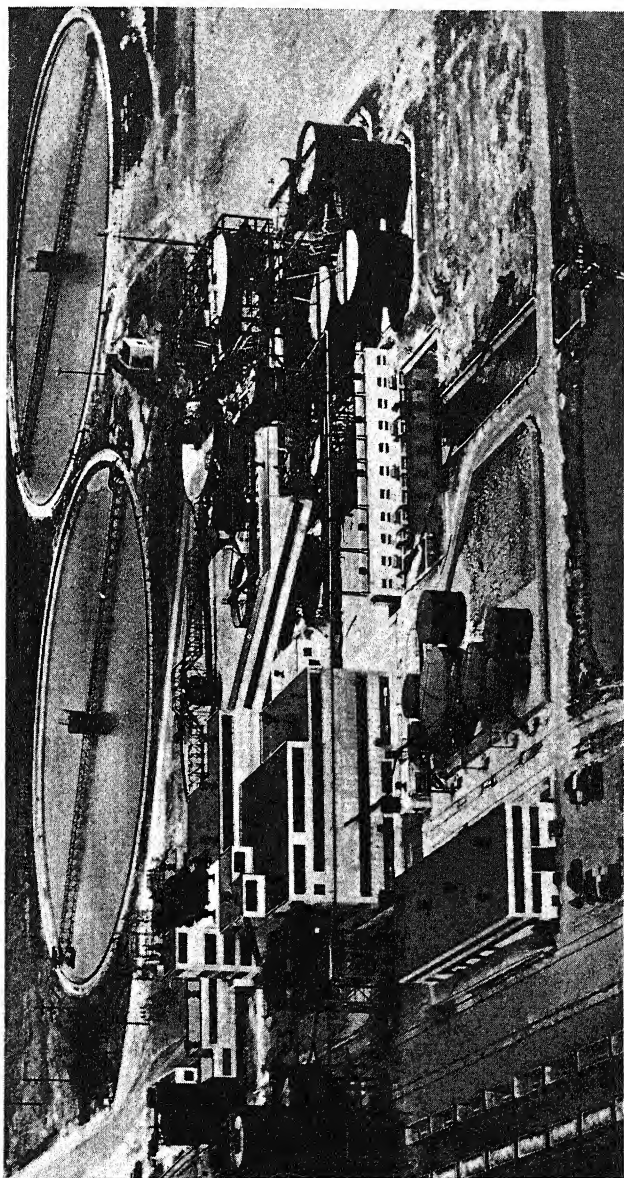
FIGURE 12. Aerial view of the Noralyn Plant of the International Minerals and Chemical Corporation, near Bartow, Florida.
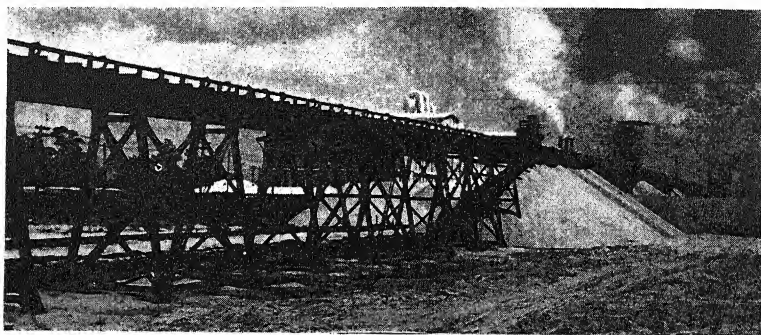
(Courtesy of Int. Minerals & Chem. Corp.)

FIGURE 13. Trestle for distributing washed pebble phosphate to storage piles. This rock is later taken to the dryer and finally to dried rock bins from which it is drawn for shipment.
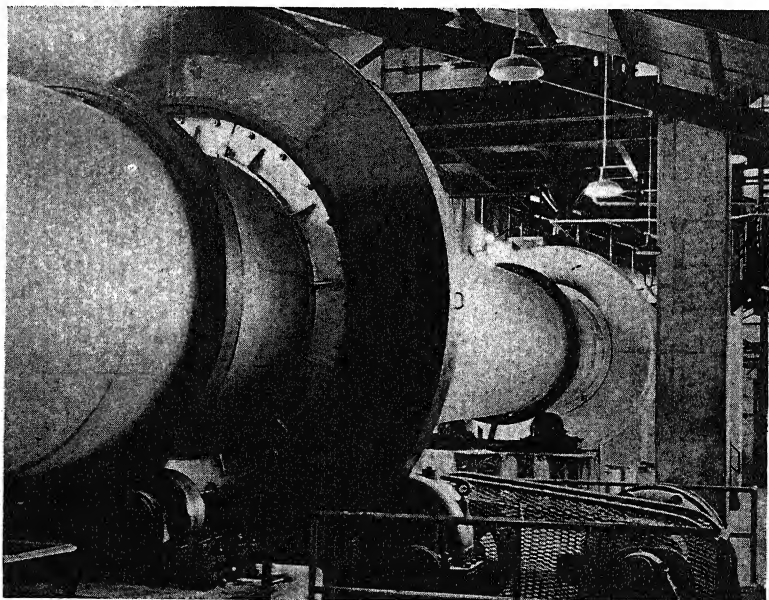
(Courtesy of Int. Minerals & Chem. Corp.)

FIGURE 14. Rotary cylindrical dryer for reducing moisture content of pebble phosphate preparatory to shipment.

plant of International Minerals and Chemical Corporation of an 8 by 80 foot dryer. The use of single large dryers has increased the efficiency and has cut the cost substantially.

Since the feed to the dryer is taken from wet storage, the moisture content will vary with the weather. During the summertime when heavy rains fall nearly every afternoon, the content may be as high as 15 per cent. However, long period averages indicate approximately 11 to 12 per cent as an average moisture in concentrate feed.

The moisture in the coarse pebble rock will be higher. Because of the longer time required to dry the coarser pebble, a drier will have less capacity drying coarse pebble than when drying concentrates. Phosphate shipped ordinarily carries a guarantee of a maximum of 3 per cent moisture.

All driers in the phosphate field are operated on Bunker C fuel oil. The consumption of fuel oil per ton of rock dried will vary with the drier installation and with the percentage of coarse pebble in the material. A drying plant includes the auxiliaries such as the boiler for preheating the fuel oil, the dust collection system, and the auxiliary conveyors and elevators.

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6. The Phosphates of Tennessee

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Tennessee has maintained a position second only to Florida in the production of phosphate rock. Much work has been done in these fields and numerous valuable historical, geological and technical articles have been published on these deposits[1, 2, 3, 4, 7, 9, 11]. A brief description of the deposits, their mode of occurrence, and the system of mining and beneficiating employed is given in this chapter in order to show their economic relation to industries using this mineral as a raw material.

The development of other processes for producing phosphoric acid and elemental phosphorus has now placed Tennessee phosphates in a position where they are only partly dependent on the fertilizer industry for a market. Large supplies of low cost power have attracted to the Tennessee phosphate field a relatively new and highly important supplement to the fertilizer industry in the form of electric furnace plants for the production of elemental phosphorus. Since such plants can utilize lower grade rock than is considered suitable for the manufacture of phosphatic fertilizers by the conventional acid process, the life of the Tennessee fields has been greatly prolonged.

Tennessee is well situated for the distribution of fertilizer material to the southern and middle western states and is conveniently near the manufacturing industries consuming large quantities of phosphorus, phosphoric acid and phosphates. Its phosphate deposits occur in what is known as the Central Basin of Tennessee (elevation 600 feet) and in the valleys of the western part of the Highland Rim (elevation 1,000 feet) surrounding the basin, an area of approximately 7,000 square miles of gently undulating country. The phosphate deposits have been developed in the western part of this area, and only a portion has potential phosphate-producing value. The mines producing at present lie in Maury, Giles, and Hickman Counties, but deposits have also been mined in Davidson, Lewis, Perry, Sumner, and Williamson Counties. The main streams in the phosphate region are the Cumberland, Duck, and Tennessee Rivers, but there are several creeks and tributaries of the Duck River that are important sources of water supply for mining and washing the rock. The phosphate area is served by one railroad, but good county and state roads enable motor vehicles to operate freely in the district.

There are four types of phosphate rock in Tennessee, namely, nodular (or kidney), brown, blue, and white phosphate. Nodular phosphate has no economic importance despite the fact that it was the first type to have been identified (1888) as a phosphate mineral in Tennessee. Blue and white phosphates are not being mined at this time, although they have future economic possibilities.

Brown Rock Phosphate

All of the Tennessee brown rock phosphate occurs in rocks of Ordovician Age, but there are numerous phosphate horizons in this series which frequently occur so close together that they may be mined as a single bed. According to Hayes and Ulrich[4] the stratigraphic succession of the phosphate-bearing formations are given in Table 1.

Brown rock is believed to be residual deposits left from the weathering of phosphatic limestone once existing in overlying formations. When these formations were close enough to the land surface to be within the sphere of weathering agencies, the more soluble limestone was leached out by percolating water, leaving a residue in which the less soluble fluoapatite was concentrated in proportion to the limestone removed. In most cases, the remaining $CaCO_3$ is low, indicating that this phase of the natural concentrating process was essentially complete. There are many evidences of secondary enrichment in the area, but the quantity of phosphate is relatively small.

Two distinct forms of deposits have been recognized, namely, collar (hat band) and blanket deposits. The first type occurs as remanents of the horizontal phosphatic limestone stratum outcrop on the slope of a steep hill. Under these conditions, the parent rock has been leached at the outcrop and the core of the hill unaffected by percolating waters. These deposits seldom, if ever, are traceable through the hill and rapidly decrease in thickness as mining progresses away from the outcrop. The blanket deposits, on the other hand, sometimes cover wide areas and usually lie near the surface of gently undulating hills where the underdrainage has been favorable to the action of percolating waters. Favorable conditions for the formation of this type deposit exist in Maury County near Mt. Pleasant and in Williamson County near Franklin. The Williamson County deposits generally are quite sandy and contain very little phosphate cemented into lump form. The brown phosphate varies in color from a light gray to a deep chocolate brown and in texture from a porous rock disintegrating into phosphatic sand to a hard close grained rock quite resistant to weathering. On the average, however, the matrix, as it is now commonly called, consists of brown to gray plates mixed with larger quantities of gray to red and brown phosphatic sand and clay. This matrix ranges in thickness from a
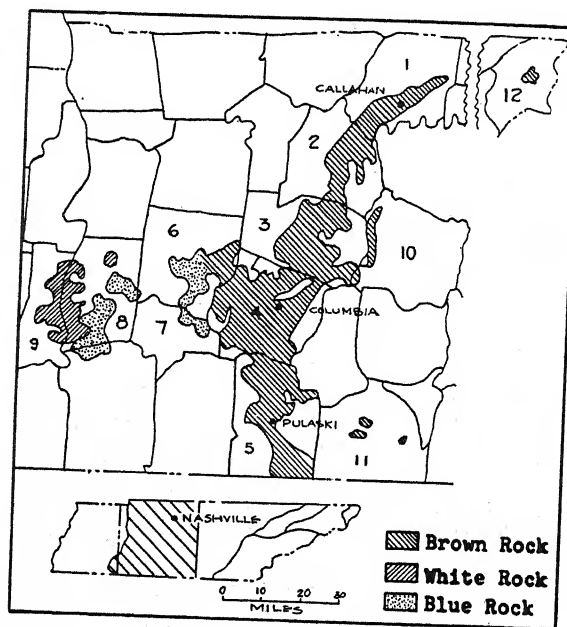
Phosphate Rock Counties of Tennessee

1. Sumner
2. Davidson
3. Williamson
4. Maury
5. Giles
6. Hickman
7. Lewis
8. Perry
9. Decatur
10. Rutherford
11. Lincoln
12. Johnson

FIGURE 1. Distribution of three types of phosphate rock in Tennessee. (*Tennessee State Geological Bulletin 48*)
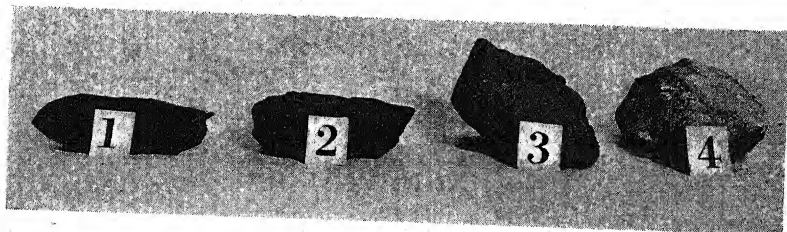
(*Tennessee State Geological Bulletin 48*)

FIGURE 2. Four types of Tennessee phosphate rock: (1) Nodular (kidney) phosphate—heavy, dense, and nearly black in color and found in Maury green shale in boulder form. (2) Blue rock—heavy, coarser in grain size than (1), showing bedding planes and blue in color. Usually contains FeS_2 which on surface deposits oxidizes and stains portions of the sample brown. (3) Brown rock—not so massive, somewhat porous, tan to gray in color. (4) White rock—heavy, massive, hard with knurly structure. Color—pink, red, gray, white, and pale green blotches.

few inches to 20 or 45 feet with an average of from 6 to 8 feet. The overburden varies considerably in places, even in the same deposit, and mining is usually discontinued when the ratio of overburden to phosphate exceeds 5 to 1.

Prospecting[1]

Brown rock values were formerly estimated by sinking a few carefully located pits about 3 by 5 feet in size, sampling the exposed matrix, and using a large factor of safety in the subsequent calculations. Later, 4-inch post hole augers were used, strengthened by reinforcing the lower cutter edges and operated by hand.

Since World War II, manually operated drilling has proved too costly and portable motor-driven drills have been adopted. Two types of power

TABLE 1. GEOLOGIC FORMATIONS IN WEST-CENTRAL TENNESSEE WHICH CARRY BROWN ROCK PHOSPHATE

Age	Formation	County Where Found
Ordovician	Leipers formation	Lewis, Hickman, Sumner
	Catheys formation	Maury, Hickman (unimportant)
	.....*	.....
	Bigby limestone	Maury, Giles
	Hermitage formation	Maury, Williamson, Davidson

* According to R. W. Smith of the *Tennessee Geological Survey*, a formation known as the Cannon occurs between the Bigby and the Catheys formations which has given rise to several important phosphate deposits in Williamson and Davidson Counties.

drills, both truck mounted, are being used. One has an augering bit and stem which may be used either with or without casing. Much of the sample is conveyed to the surface by this machine and the rest of the cuttings elevated with the tools when the hole has been completed. This drill is fast and excels in drilling through overburden. Several types of tools are available and satisfactory results may be expected when used by skilled operators. The other drill, designed for geological investigations of oil structures, can operate wet or dry, and is provided with a greater variety of attachments and bits. It may be used to take a core sample in either hard or soft material and its most attractive feature is the ability to sample the matrix with a minimum of contamination from overburden when used in an uncased hole. The core barrel may be either 5 or 10 feet in length, and although the string of tools must be pulled and the core recovered more often than the augering type, a more representative sample is obtained with this method.

It is customary to sample the matrix shown in the holes at 4-foot intervals. Washing tests and chemical analyses are then run on composite

samples and from these data the total tonnage and grade of the deposit in a given area are calculated. Areas where the depth of the overburden

FIGURE 3. Flow sheet phosphate washing process in Tennessee.

exceeds that of the phosphatic matrix by 4 or 5 times are usually considered uneconomic to mine even though the matrix may be of usable grade. Most companies evaluate their phosphate reserves in terms of long tons and use the same unit on sales quotations.

Mining and Beneficiation

For a number of years after the discovery of these deposits, mining methods employed were both crude and wasteful, no attempt being made to recover anything but the highest grade plate rock. As the available supply of such plate rock diminished, however, advances were made in both mining and beneficiating phosphate sand and greater efficiency was attained[2, 11].

Just prior to and during the early years when the electric furnace industry was being established in Tennessee, froth flotation methods were
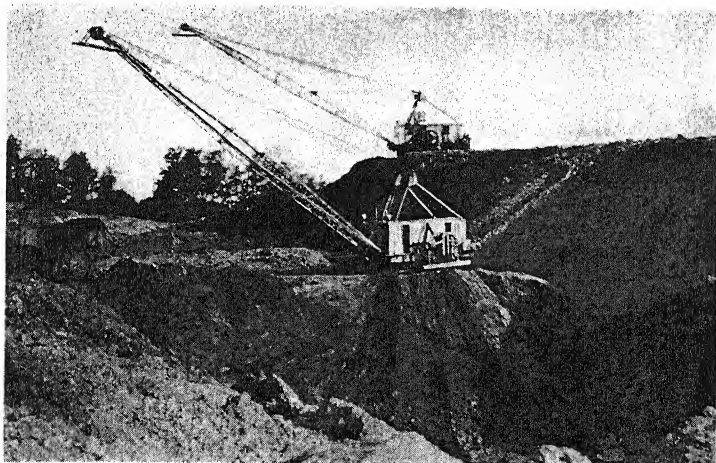
(Courtesy of Monsanto Chemical Co.)

FIGURE 4. Strip mining of Tennessee phosphate rock. The upper dragline is stripping off the overburden, while the lower dragline is mining the phosphate strata thus exposed.

employed to concentrate low-grade phosphate sands. When it was found that much of this siliceous phosphate could be used directly in electric furnaces to produce elemental phosphorus, beneficiation of this low-grade material by flotation was largely abandoned. The bulk of the deslimed phosphatic sand on which the flotation process works best has now been diverted to furnace use although an appreciable tonnage is ground (90 per cent through a 200-mesh screen) for direct application to the field. Three grades of phosphate now find ready markets: fertilizer and acid grade, 68 to 74 per cent BPL; ground rock for direct application, 66 per cent BPL; and furnace grade, 50 to 60 per cent BPL.

Under present conditions, the overburden is first, stripped by means of a dragline and the phosphate strata exposed is removed by a dragline in

much the same way that Florida pebble phosphate is handled. It is common practice to remove the overburden well in advance of mining by using two draglines simultaneously.

The phosphate matrix, consisting of varying proportions of lump rock and phosphatic sands, is mined and transported to the washer by truck, tram, railway, or pumped as a slurry of water and matrix. The majority of the companies transport by truck or contract for haulage by privately owned dump trucks. Several of the companies are experimenting with and using trucks capable of handling 10 or more yards, but practically all of the contract haulage is in 2 to 4 yard units. Figure 3 shows a flow sheet of the TVA washing plants, one of the most recent installations in the field. It contains many features and mechanical devices common to other plants. Matrix is mined and delivered by the dragline bucket to a portable hammer-mill, water is added, and the crushed slurry is caught in an open sump dug near the hammermill. A centrifugal pump sucks the slurry from the sump and delivers it by means of a steel pipeline to a screen at the washing plant. The oversize goes to a ball mill operated as a scrubber and having a trommel screen attached to the discharge end. Any oversize from this screen goes to a similar ball mill installation provided with a belt conveyor, keeping the oversize in closed circuit until satisfactorily disintegrated. No steel balls are used in these mills as they tend to slime the soft phosphate, and very satisfactory results have been attained by using the occasional lumps of limestone, chert, and phosphate normally found in the matrix as grinding media. When the load of limestone and chert becomes excessive, the mill is dumped by removing the manhole cover and rotating the mill a few turns. The fines passing the first screen and those in the ball mills collect in a sump and are pumped to a sand washer which mechanically separates the pebble rock and sand at about 60 mesh. The −60 mesh sands, together with most of the water, flow to a hydroseparator. The finely divided clay and very small particles of phosphate gradually work to and overflow a level baffle around the circumference of the tank and are drained by gravity or pumped to mud ponds as a waste product. The larger phosphate and silica sands settle to the bottom of the hydroseparator, are plowed to a central bottom discharge, and after being continuously mixed with the pebble product from the sand washer are pumped to the classifying plant at another location. The 8-inch steel pipeline between these plants is approximately 16,000 feet long and is equipped with three motor-driven centrifugal pumps. Two pumps are placed near the hydroseparator and by-passes are provided in the line so that either may operate independently of the other. A third centrifugal pump, essentially a booster pump is placed about one-third of the way along the pipeline toward the classifiers. This

combination enables continuous pumping, even though one pump unit may be out of use for maintenance or other reasons.

The classification plant consists of a rake, bowl, and centrifugal-type classifiers. Three sand products ranging in size from minus 1 inch to plus ten microns are regularly recovered. The products from the rake and bowl classifier are collected in conical piles for 24 hours and then removed by an electric track crane to an open storage yard. The product from the centrifugal classifier is too wet and the particle size too small to pile immediately after recovery, so it is collected in a concrete sump. Water is decanted and
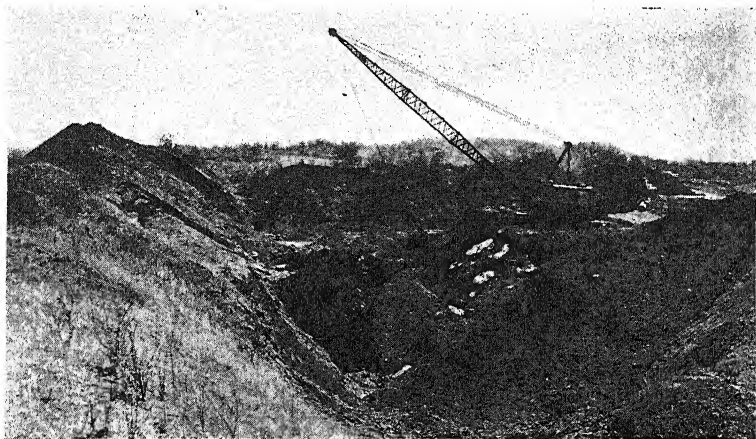
(Courtesy of Monsanto Chemical Co.)

FIGURE 5. Scrap mining. This is a view of an area near Mt. Pleasant, Tennessee, that was thought to be mined out. The dragline is now remining the richer sections and the matrix is hauled by truck, shown in the background, to a washing plant. This is now an uncommon practice in Tennessee.

the thick settled sand removed daily to storage by a clam-shell bucket. The feed to the centrifugal classifier is the underflow from a hydroseparator which, in turn, is fed by the bowl classifier overflow. Until the market was established for electric furnace feed, this fine material would not have been worth saving, and no attempt was made to recover particle sizes smaller than 200 mesh. Higher grade concentrates which are suitable for fertilizer purposes, either as ground rock for direct application or to be acidulated, are dried in rotary kilns using coal as fuel. Electric furnace feed is prepared by blending raw matrix with low-grade washed sands without drying. The material is then sent to either sintering machines or nodulizing kilns where it is dried and agglomerated, screened, and held in dry storage until charged to the furnaces.

Probably more than half of the phosphate mined in Tennessee is used locally by the three electric furnace operations, two of which have been installed in the heart of the producing area, while the third is about 80 miles away in northern Alabama.

Larger quantities of iron and aluminum oxides are acceptable for electric furnace treatment than phosphate rock which is to be acidulated. In the former case, however, practically all the iron in the charge is reduced to ferrophosphorus, for which there is a limited market, and hence more
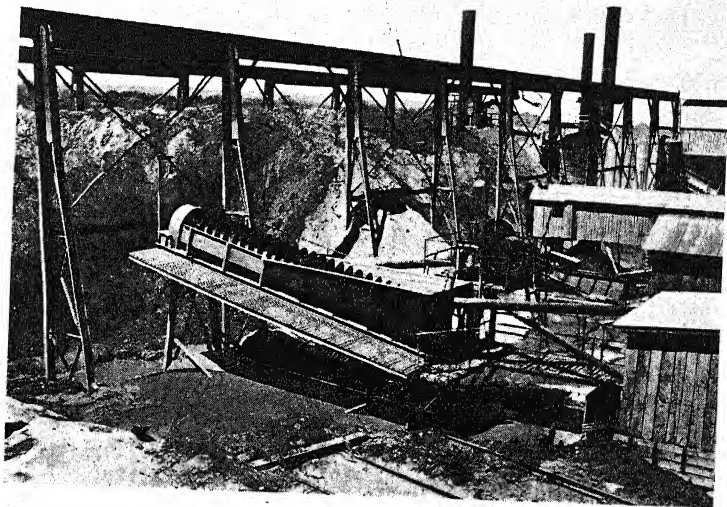
(Courtesy of TVA)

FIGURE 6. Modern screw classifier with storage pile in background. Overhead crane with clam shell bucket puts in and withdraws washed phosphate from storage. The machine shown is used here as a dewatering device.

than 4 or 5 per cent as Fe_2O_3 is considered objectionable. Export shipments are no longer common, and few shipments of rock or sand are transported more than a few hundred miles from the place of origin.

While efficient mining and washing of brown phosphate rock involves considerable capital investment,, the percentage of recovery with modern mechanical equipment is so much greater than it was formerly when the value of phosphate sand was unknown or unappreciated, that the cost of production has been maintained at a relatively low figure. Moreover, were it not for this mechanical equipment and the advent of conditions suitable to electric furnace operation, the Tennessee brown phosphate fields would have been largely abandoned by this time due to exhaustion of the bulk of the high grade lump rock and sands.

Blue Phosphate

Blue rock was first identified as a phosphate ore in 1893. The discovery was made on Swan Creek at a point about 22 miles west of Columbia. Smith and Whitlatch[10] describe it as follows:

"The blue rock phosphate is an unaltered phosphatic portion of the Hardin sandstone member of the Chattanooga shale of basal Mississippian age. It occurs in Hickman, Lewis, and Maury Counties along the edge of the Highland Rim on the southwest side of the Central Basin; areas of less commercial importance occur in Perry and Wayne Counties. Its thickness varies from a few inches to three or four feet. The composition of the rock ranges from a somewhat phosphatic shale or sandstone to a dense, highly phosphatic rock.The richest blue rock is often oolitic-like in appearance. The shaly and conglomerate varieties are too low in grade to be of much current economic value. They are shales, sandstones, and conglomerates with a phosphatic content up to 45 or 50 per cent BPL and represent gradations between commercial blue phosphates and the ordinary Hardin sandstone. The oolitic and compact varieties of blue phosphate may contain up to 75 per cent BPL but their general average is 65 per cent. The term 'blue rock' is applied even when the rock is gray or brown in color."

The last large producer of blue rock suspended operations in 1937 and since that time there has been no blue rock production of consequence. Early mining consisted largely of removing the exposed blue rock where it outcropped along the stream beds. When the rock overburden became too thick to handle at low expense, operations were abandoned. Later tunnels and cross cuts were driven underground and the ore removed in a manner similar to the room-and-pillar system used in small coal mines[12]. Heavy piston machine drills were used to make a top cut and the phosphate seam shot by drilling in or just below the seam and breaking to the cut. Mucking was done by hand into small tram cars which were drawn to the surface by mules or pushed by hand. The total blue rock produced in Tennessee since its discovery is estimated at about 1,500,000 tons.

Recently blue rock has been experimentally concentrated[2] and most authorities, who have estimated phosphate reserves in the state, agree that a large part of the remaining phosphate reserves in Tennessee is in the form of blue rock. Interest has been renewed to the extent that definite plans have been made and modern core drilling equipment purchased to prospect certain deposits on a more comprehensive scale than has heretofore been thought advisable.

White Phosphates

White phosphates have been found in Perry, Decatur, and Johnson Counties in Tennessee. Exploitation on a small scale has been done in Perry

and Decatur Counties[5, 8] while that in Johnson County, after more thorough examination, has proved of little economic importance. This type phosphate is of Tertiary or post-Tertiary Age and is of secondary origin. Hayes[3] describes three classes, namely, the stony, breccia, and lamellar varieties, the last mentioned being the richest and most plentiful. Much of the white phosphate of Tennessee resembles the hard rock phosphate of Florida, and occurs in irregular pockets along with clay and other foreign material. The breccia variety consists of chert fragments imbedded in matrix of high grade phosphate, while the stony phosphate consists of siliceous skeletons formerly filled with carbonate of lime, but now containing phosphate. Both of these varieties must be freed of the associated chert in order to yield a commercial product, but up to the present the cost of effecting such a separation has not warranted their exploitation. The lamellar variety of white phosphate, however, is a high grade material occurring in plates of various thickness, frequently pink or red in color and cemented together, forming large boulders. The rock is close grained, hard, and often coated with a thin lustrous layer of precipitated phosphate locally called turkey fat. Picked samples of lamellar phosphate may contain 85 per cent or more of bone phosphate of lime and it has been mined in carload lots containing from 70 to 78 per cent BPL.

While no development work is being conducted in white phosphate fields at present, the rock was formerly mined by both open-cut and underground methods. The former method was employed wherever the character and depth of the overburden would permit, but the overburden was frequently so heavy as to render its removal unpracticable by hand or mule-drawn scraper and underground methods were used. Owing to the loose, and frequently wet character of the overlying clay, extensive timbering was required, which added considerably to the cost of production.

Tennessee white rock exploitation ceased in 1908 but was revived for a time when the Tennessee Valley Authority resumed open-pit mining in Perry County in 1934 by use of a diesel-driven power shovel. The rock was selectively mined and sun dried; the clay either fell free from the phosphate or was largely eliminated by hand labor and coarse screening. The rock was shipped in barges up the Tennessee River to Wilson Dam. This last operation was seasonal but the small quantities of rock found in the deposits, together with the difficulty of finding new ones closed down the operation in 1936. In all, about 25,000 tons of white phosphate have been mined to date, of which more than 15,000 tons were produced by the TVA's venture in this field.

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7. Western Phosphates

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INTRODUCTION

The western or Rocky Mountain phosphate field embraces outcrops of phosphate-bearing rocks covering an area of 100,000 square miles in portions of Idaho, Montana, Nevada, Utah and Wyoming. Reserves of mineable high-grade rock (31.5 per cent P_2O_5) have been estimated at 7,985,000,000 long tons[6]. This estimate includes all rock lying at depths less than 5,000 feet below the surface. A recent preliminary estimate has been made that not more than 1,000,000,000 tons of the above reserve lie in deposits considered to be economically mineable under present practices (i.e., above adit level)[8]. Reserves of low-grade rock (phosphatic shales), roughly estimated in terms of tens of billion tons, have not been computed.

The first discovery of phosphate rock was recorded in Cache County, Utah, in 1889. Mining was begun on the western deposits near Montpelier in 1906. Early mining operations were confined to the deposits in the Bear River region of Idaho, Utah and Wyoming because of their richness and proximity to railroad transportation.

Although the extent of the western deposits was approximately outlined by geological studies made by the United States Geological Survey during the period 1906 to 1927, commercial development progressed slowly because of relatively high transportation costs to fertilizer markets. As deficiences of available phosphate were discovered in the cultivated soils of the intermountain and western coastal states, a western market for phosphate fertilizer was developed and the tempo of western phosphate mining operations increased rapidly during the past twelve years (Figure 1).

The western field is now producing approximately 10 per cent of the total United States phosphate rock, as compared to 2.3 per cent produced in 1936.

CHARACTER AND THICKNESS OF DEPOSITS

The western phosphate deposits are of sedimentary origin and lie at two distinct geological horizons, one in the upper Mississippian and the other in the Permian. Only the latter are of sufficient thickness and grade to be of economic importance at the present time. The beds were originally

deposited in horizontal or nearly horizontal layers but have been severely folded and faulted by crustal deformations during the Cretaceous Period. Local sections now dip at any angle from nearly horizontal to vertical. Subsequent erosion has exposed the phosphate-bearing formations in narrow bands along the flanks of the simpler folds or as irregular fringes in the
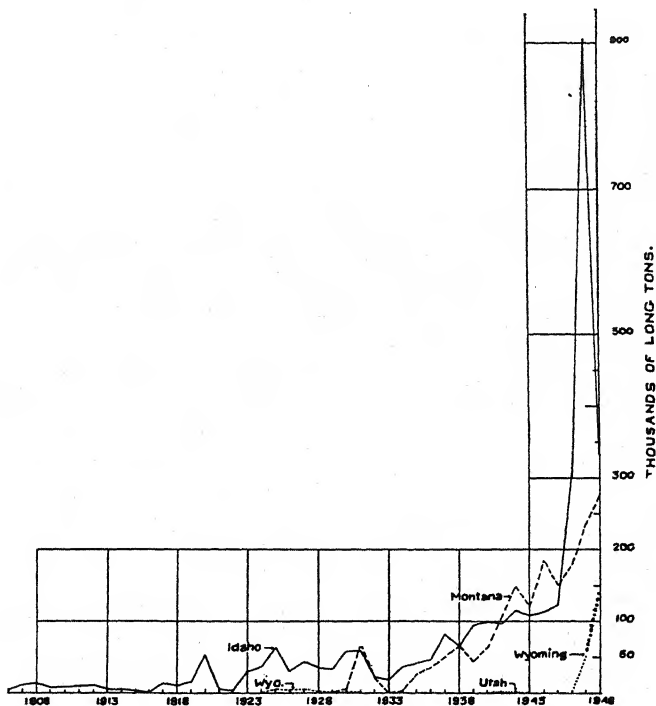
FIGURE 1. Production of phosphate rock from Idaho, Montana, Wyoming and Utah during the years 1906 to 1948 inclusive. Compiled from U. S. Bureau of Mines Statistics.

more complex folded and faulted areas. The geologic structure of the eastern portion of the Permian deposits in Wyoming and eastern Utah is characterized by gently dipping and widely spaced folds in which faulting movements have been comparatively infrequent. In the western portion of this field the structure becomes more complex. Sharp folds are closely spaced and often overturned. The beds dip steeply and faults of large and small displacement are frequent. Occasionally the beds are doubled up or thinned out by the effect of compressive forces of folding and the resultant strike faulting.

The Permian Phosphoria formation contains two distinct lithologic units. The upper unit, known as the Rex Chert member of the Phosphoria, consists mainly of massive siliceous limestones and cherts, sometimes grading to quartzite and conglomeratic phosphatic chert in western Montana. This unit varies from approximately 40 to 550 feet in thickness, and is generally characterized by massive siliceous rocks that are resistant to weathering and often form bold outcrops which serve as a marker element for the Phosphoria series. The Rex Chert contains traces of phosphate throughout its thickness and occasionally higher grade material occurs in thin seams. The lower unit, known as the Phosphatic Shale member of the Phosphoria in southeast Idaho and adjoining areas, consists of a sequence of seams of oolitic phosphate rock, phosphatic shales and other marine sedimentary layers, the whole sequence varying in thickness from approximately 25 to 200 feet. The Phosphoria shales are generally soft, thin-bedded, and non-resistant to weathering. Their outcrops are characterized by erosion gullies and depressions. The phosphatic shales vary in thickness, phosphate content and chemical composition throughout the field. Of the developed or partly developed areas, the Bear River region in southeastern Idaho and adjoining parts of Wyoming and Utah contain the thickest and higher grade deposits. Here the Phosphatic Shale member has a thickness of from 75 to 200 feet. Analyses of three complete sections in this region show respective averages of 11, 12.88 and 17 per cent P_2O_5. The thickness and phosphatic content of the shales diminish to the south, east and north of this region. To the west, sections of the Phosphoria beds have been identified near Malta, Idaho[2], in the Confusion Range in western Utah[9] and in the Goshute Mountains in Nevada, about 35 miles southeast of Wendover, Utah. Such data as are available from these westerly exposures indicate a progressive thickening of the Phosphoria formation westward from the Bear River region. The phosphate contents of the western extensions are unknown.

Complete sections of the Phosphatic Shale member, made at Conda, Slug Creek and Georgetown Canyon in southeastern Idaho[7, 9, 12] reveal that the greater part of the phosphate is concentrated in two zones near the base and top respectively of the shale series. These richer zones are composed of beds of oolitic phosphate rock and beds of thin-bedded shales and mudstones interbedded with thin seams of finely oolitic material.

HIGH-GRADE ROCK

In southeastern Idaho there are two high-grade or currently commercial beds of phosphate rock. The lower, or footwall bed, at the base of the lower phosphatic zone, ranges in thickness from 5 to 9.5 feet and varies from 32 to 33.5 per cent in P_2O_5 content. The probable average is about 7.0 feet

of 32 per cent P_2O_5 rock. Lower grade clay and shale partings are present in this bed but are not numerous or thick enough to dilute appreciably the mined-grade of rock. This bed is often overlaid by a bed of hard fossiliferous, phosphatic limestone 1 to 3.5 feet thick, known locally as cap rock or cap lime.

The upper, or hanging-wall bed, lies near or at the top of the upper phosphatic zone, close to the Rex Chert. This bed ranges in thickness from 5 to 7.5 feet and varies from 30 to 35.5 per cent in P_2O_5 content. A general average of thickness and grade cannot be estimated for this bed. Even at Conda, Slug Creek and Georgetown Canyon, the oolitic layers are interbedded with seams of limestone and/or mudstone, which lower the grade of the rock as mined. Farther south, as in the Beckwith Hills area, the upper bed contains fewer low-grade partings and is hard, dark colored and massive, and assays from 32.5 to 35.5 per cent P_2O_5 across thicknesses of 5.0 to 5.5 feet.

High-grade rock is dense and characteristically oolitic, or partly nodular; sometimes the original grain of the rock is altered or destroyed by compression or by shearing. The oolites are rounded grains of concentrically layered phosphatic material which range from particles that pass 80-mesh screen openings up to ovules of half-inch diameter. The oolites are cemented together by fine grained (-150 mesh) material that generally contains from 15 to 22 per cent P_2O_5. Below the zone of surface oxidation the rock is highly carbonaceous, brownish-black to bluish-black in color, and gives off a bituminous or fetid odor when broken. Near the surface the rock has been oxidized and weathered to a lighter color, varying from light gray to cream through darker shades of gray or brown. Outcrops are characteristicly weathered to a light bluish gray. Weathering reduces the carbonaceous and calcareous contents of the beds, thereby increasing the percentage of tricalcium phosphate through residual effect.

In the Beckwith Hills-Crawford Mountains region the lower bed is either absent or leaner than in southeastern Idaho. In Montana the lower bed is absent or is thin and low-grade except in the Snowcrest and Centennial Ranges, where prospects of commercial grade rock have been found. In the Garrison-Avon-Elliston area the upper bed occurs at the base of the Phosphoria formation because of the absence of the lower members. The bed is from 3 to 5 feet thick and contains from 32 to 34 per cent P_2O_5, except where it is occasionally contaminated by interbedded silty partings which reduce the average phosphate content. In the Maxville-Philipsburg area the upper bed is from 3 to 4 feet thick and frequently contains interbedded aluminous or siliceous seams which cause a variation of phosphate content ranging from 32 to 22 per cent P_2O_5. In the Melrose-Divide area there are two seams of high-grade phosphate rock interbedded with 1.5

feet of highly siliceous shale or argillite, the mineable width of which is approximately 6 feet, averaging about 25 per cent P_2O_5.

The high-grade phosphate rock has a specific gravity varying from 2.80 to 2.95; the average for 32 per cent rock is about 2.90. The rock consists essentially of tricalcium phosphate, with appreciable quantities of silica, organic matter, calcium in excess of the requirements of the calculated $Ca_3(PO_4)_2$, and minor quantities of alumina, iron, fluorine, sulfur and many trace elements, the most important of which up to the present time is vanadium. Vanadium is precipitated and recovered from phosphoric acid

TABLE 1*

	I (%)	II (%)	III (%)	IV (%)	V %)	VI (%)	VII (%)	VIII (%)
P_2O_5	30.30	31.60	32.30	32.10	36.35	25.50	32.20	34.70
SiO_2	7.80	4.40	5.10	11.00	0.30	23.90	12.40	7.20
Fe_2O_3	0.90	1.00	0.90	0.87	0.26	2.70	1.35	1.20
Al_2O_3	1.30	1.65	1.50	1.70	0.50	4.00	1.25	1.00
SO_3		2.30	1.20		2.98	1.05	0.95	0.55
CaO	45.40	47.10	47.00	45.50	50.97	33.80	44.90	47.80
V_2O_5	0.26	0.29	0.23	0.12		0.11	0.08	0.21
F	3.81	3.50	3.60	3.60	0.48	2.60	3.55	4.48
MgO		0.57	1.20		0.22			0.25
Na_2O		0.78	0.50		2.00	1.40		0.07
CO_2		2.23	2.80		1.72	1.30	0.90	
Ign. loss	7.25	5.86	6.50	2.90		2.80	1.50	1.75

* I to III, Idaho samples; IV and V, Utah-Wyoming samples; VI to VIII, Montana samples.

Additional determinations made on one of the Idaho analyses are as follows: As_2O_3—0.003; TiO—0.11; Cr_2O_3—0.15; CuO—0.023; MnO_2—0.011; ZnO—0.12; K_2O—0.37; Ag—Tr.; Au—Nil.; U—0.01. Two of the Montana samples had Cr_2O_3 determinations of 0.14 and 0.04 per cent respectively.

solution during the process of acid phosphate manufacture at Anaconda, Montana. Data on chemical composition of the phosphate rock are incomplete except in a few localities where extensive mining has been carried out. Some typical analyses of oolitic phosphate rock as mined from some of the active mining districts in the western states are given in Table 1.

Low-Grade Rock and Phosphatic Shales

Low-grade western rock includes all classes of material that analyze from 30 to 15 per cent P_2O_5. Oolitic phosphate beds, interbedded with lower grade seams, fall into this category, although the term low-grade rock usually applies to the phosphatic shale beds that lie respectively above and below the lower and upper oolitic phosphate beds. These phosphatic

shales consist of a sequence of marine sedimentary beds of varied thicknesses whose characteristics are determined by their relative contents of silica, calcium carbonate and alumina or other contaminants. These beds have been enriched in some degree by phosphatic material precipitated during the silting process. The distinguishable layers vary from a fraction of an inch up to 12 feet or more in thickness and the phosphatic content ranges from 1 up to 30 per cent P_2O_5. The beds are characteristically fine-grained in texture and stratification varies from thin-bedded shales or argillite to thick-bedded and often massive impure limestone and mudstone. Clay partings often mark the transition between layers. The color was originally dark-brown to black, but where oxidation and leaching have occurred, varying shades of brown, light yellow and light gray have resulted. Of the areas developed, the phosphatic shales are of commercial importance only in southeastern Idaho, southwestern Wyoming and in north central Utah. In these areas there are usually one or two groups of adjacent or proximate beds containing from 20 to 29 per cent P_2O_5 aggregating from 5 to 25 feet in thickness. These groups are found in the lower and upper phosphatic horizons near the base and top, respectively, of the Phosphatic Shale member of the Phosphoria series. Analyses of a few Idaho and Wyoming shales are given in Table 2.

Possibilities of Commercial Exploitation of Phosphatic Shales

The total phosphate content of phosphatic shales is at least four times that of oolitic phosphate rock beds. Until recently the shales have not been of commercial importance because the cost of mining has been approximately the same as for the higher grade rock. The surface stripping operations at Montpelier and Fort Hall, Idaho[4], and at Leefe, Wyoming, have recently made available large quantities of phosphatic shale, which can be mined at comparatively low cost because production is supplementary to the mining operations for high-grade rock. The availability, in the western phosphate field, of cheap electric power and large tonnages of phosphate rock and phosphatic shales, containing about 25 per cent P_2O_5 and a favorable silica-lime ratio, has recently (since 1948) brought about the construction of three electric furnaces for the production of elemental phosphorus near Pocatello, Idaho. Another furnace is now in operation at Silver Bow, Montana.

Considerable experimental work has been done on the beneficiation of phosphatic shales by several of the mining and fertilizer manufacturing companies and by the University of Idaho[3, 10]. During October 1950 a washing plant for the beneficiation of phosphate rock from the hanging-wall bed was put into operation at Conda, Idaho. This plant was designed to wash out part of the interbedded aluminous and siliceous material and

to raise the phosphate content of the concentrates to above 32 per cent P_2O_5.

Further developments in electric furnace processing and in the beneficiation of the lower grade phosphatic material can be expected within the next few years.

TABLE 2*

	I (%)	II (%)	III (%)	IV (%)
Insoluble	2.5	3.4	1.5	1.3
P_2O_5	24.15	23.4	25.4	28.75
SiO_2	27.10	24.3	19.7	18.2
CaO	33.7	30.6	38.1	38.65
Fe_2O_3	1.4	1.8	1.1	1.2
Al_2O_3	2.7	3.8	1.5	2.1
SO_3	1.4	0.9	2.2	2.07
CO_2		0.2	3.9	
Na_2O	0.7			1.1
K_2O	0.8			0.9
MgO	0.4		1.2	0.24
MnO	0.08		0.06	
V_2O_5	0.26		0.19	0.32
As_2O_3	0.0008		0.10	
F	1.7		2.30	2.46
Ignit. loss	3.9	11.0	8.5	3.85

* Analyses of typical phosphatic shales from Idaho and Wyoming.

MINING METHODS

Surface Stripping

Surface strip mining operations were initiated in the western field during the spring of 1945 by the San Francisco Chemical Company at the Waterloo Mine, 4 miles east of Montpelier, Idaho. During the following two and a half years this company mined and shipped 650,000 tons of high-grade rock from this property[5]. Here the lower (footwall) phosphate bed and 20 to 30 feet of phosphatic shales lie on the west limb of an anticline, dipping from 20 to 35 degrees to the west. The upper shales, upper phosphate bed and Rex Chert have been cut out by erosion. The remaining Phosphoria formation is covered by 15 to 30 feet of surface detritus. The slope of the hill is less than the dip of the beds, and the overburden increases rapidly toward the base of the hill. A series of cross faults has induced erosion gullies which have produced a saw-tooth pattern to the Phosphoria outcrop along the upper levels of the hillside. Stripping operations were carried on in panels, beginning at the lowest point at which overburden could be

economically coped with. Before stripping began, the entire hill slope was prospected with diamond drill holes and the size, location and sequence of panels laid out so that overburden could be wasted downhill into mined-out areas. The surface detritus and shales were stripped off by 18 to 20 cubic yard scrapers pulled by D8 Caterpillar tractors. After removing the
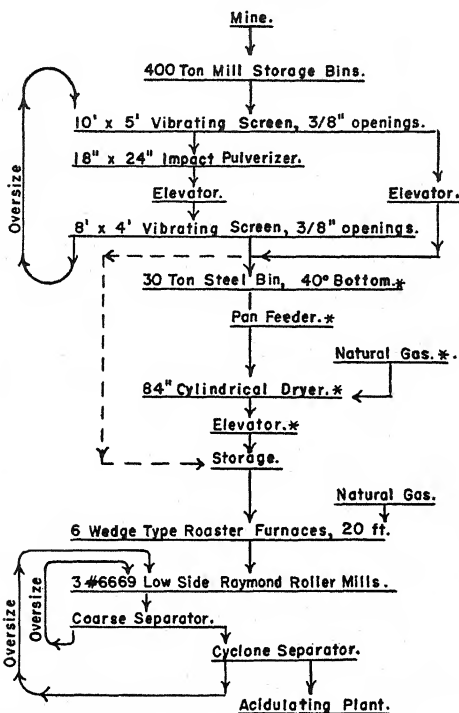
FIGURE 2. Typical flow sheet of western mill treating phosphate rock for double acidulation.

* Can be by-passed during non-freezing weather.

hard limestone cap rock (22 inches thick) by power shovels, the footwall phosphate bed was stripped off by small power shovels and loaded into dump trucks for transportation to the rail head at Montpelier. During the fall of 1947 the principal operations of this company were transferred to the Beckwith Hills deposits, about $3\frac{1}{2}$ miles west of Sage, Wyoming. Here the phosphate beds dip at a low angle through the upper portion of a series of low flat-topped hills, lying on the east side of the Bear River Valley. The Phosphoria formation has been eroded from elevations below

6,300 feet, leaving a series of nearly elliptical phosphatic areas on the higher ground, separated from one another by erosion channels.

A series of east-west faults cause vertical displacements varying from a few feet up to 30 feet or more. An overburden of surface detritus, chert and hard shale, 10 to 80 feet thick, overlies the upper (hanging-wall) phosphate bed, which is 5 feet thick and averages about 33 per cent P_2O_5. Below the hanging-wall bed lies a series of phosphatic shale beds and lesser beds of oolitic rock. Data for the definition of the phosphatic area and for calculating the amount of overburden were obtained from a pattern of diamond drill holes, spaced at 200 feet centers. Panels were laid out and stripping began on the fringe areas so that overburden could be wasted on barren ground. The panel pattern will develop toward the center of each phosphatic area, in order to shorten the overburden haul to mined-out panels. The initial fringe stripping of overburden is accomplished by pushing the waste material over the rims of the hills with Caterpillar bulldozers. After a panel is cleared of overburden the high-grade bed and the shale beds are successively stripped by power shovels and loaded into 11-yard dump trucks. The high-grade rock is hauled to a crushing and grinding mill located near the center of the deposits, on the railroad spur, which has been constructed from the Union Pacific main line near Sage, Wyoming. Each shale bed is mined and stockpiled separately, pending the conclusion of beneficiation experiments now being carried on by this company. The stripping ratio of overburden to high-grade rock is reported to be approximately $6\frac{1}{2}$ to 1.

During the spring of 1946, the Simplot Fertilizer Company commerced surface mining operations on phosphate deposits outcropping on the Fort Hall Indian Reservation, 16 miles east of Fort Hall, Idaho. Here Phosphoria outcrops along the strike of a northeast fault for several miles. The beds dip from 6 to 12 degrees to the southeast. The chert, the hanging-wall phosphate bed and the upper phosphatic shale beds have been cut out by erosion, leaving the footwall bed covered with from 20 to 75 feet of phosphatic shale, siltstone and a gradually increasing overburden of detritus as the deposits are mined toward the east. The ground was explored by a grid pattern of diamond drill holes well ahead of the stripping operation, which progresses in a series of panels northward along the shallower portions of the Phosphoria. The panel size is controlled by faulted blocks, depth of overburden and topography, as it affects the location of spoils areas. The topsoil is scraped down the slopes of the ridges by Caterpillar bulldozers or by tractor and carryalls, depending on the length of the haul. The shale beds are stripped with $2\frac{1}{2}$-yard shovels and loaded into pit trucks for stockpiling. Shale beds of 24 per cent P_2O_5 grade or better are selectively mined for electric furnace feed. The lower grade shales are stock-
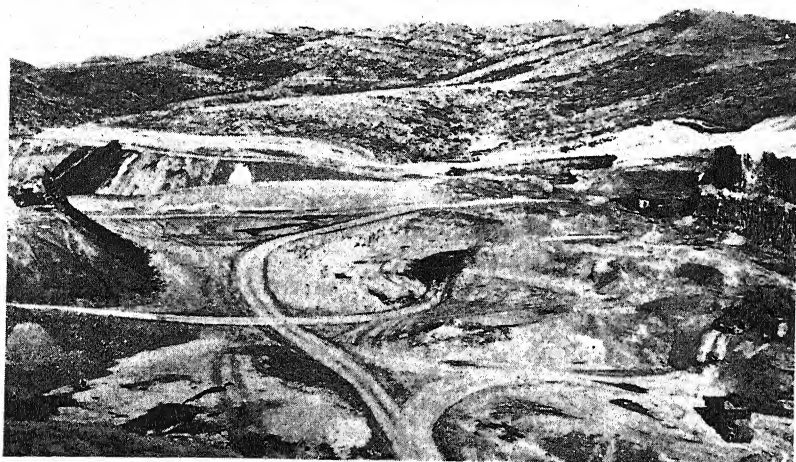
FIGURE 3. Surface mining operation of the Simplot Fertilizer Company near Fort Hall, Idaho.
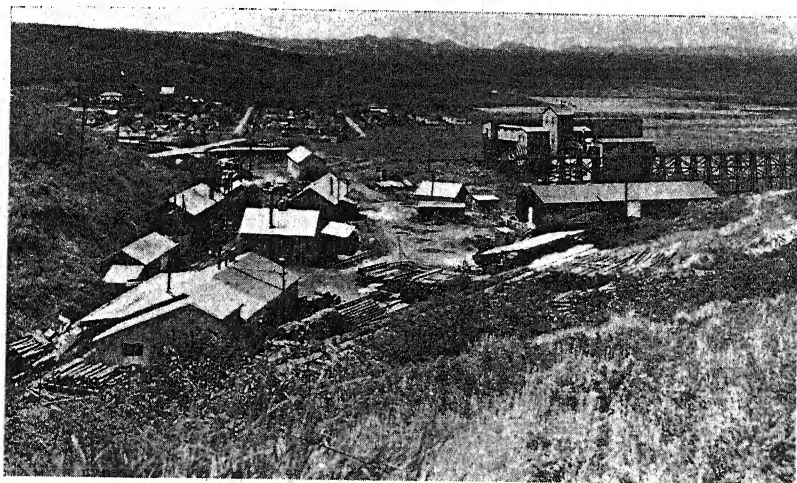
FIGURE 4. Phosphate mining town at Conda, Idaho, showing mine buildings in foreground, mill buildings at right and campsite in background.

piled separately for future beneficiation. The high-grade footwall bad, 6 feet thick and averaging about 32.5 per cent P_2O_5, is mined with $\frac{3}{4}$-yard power shovels, care being used to prevent dilution. The rock is loaded into 12-yard

pit trucks for transportation to the nearby spur line railhead. The approximate stripping ratio of waste to ore is 5 to 1[4].

Underground Mining

Underground mining operations have been conducted continuously in the western field since 1906. The mines were originally opened up as tunnel

FIGURE 5. Underground mining at Conda, Idaho, showing the south end of a sublevel, into which the phosphate rock as been blasted from the stope (showing at upper right corner). The stratified footwall phosphate bed can be seen in the center background beyond the Anaconda type scraper, which is being used to slush the broken 'rock' into the raise chutes. The hanging-wall shale, secured against sloughing by stulls and plank lagging, can be seen at upper left.

mines, but a few have resorted to shaft mining as their ore reserves above adit level diminished[1]. Several mining methods are used, depending on the type of ground and the wall conditions encountered. Where both walls are firm various modifications of room-and-pillar or stull stopes are used. In this type of stoping, raises are driven in the ore from the haulage level to the surface or to an upper level. The raises are spaced at intervals of from 75 to 250 feet, depending on the number and displacement of cross-faults encountered. Rooms or stopes are then opened up from the raises by overhand mining and the broken rock is drawn off through the raise chutes. Where the dip of the bed is less than 40 degrees, it is often necessary

to use electric slushing rigs to remove the rock. Little or no timbering is required except for drill staging. Where wall conditions permit, this is probably the cheapest method of stoping.

Where the hanging-wall is firm and the footwall soft and friable, sub-level stoping is used. Raises are spaced at intervals of 150 to 200 feet,
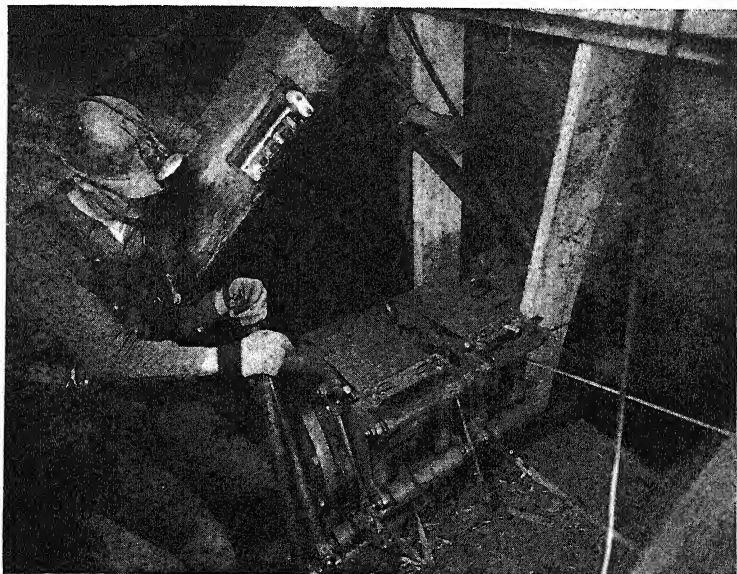
(Courtesy of the Anaconda Copper Mining Company and the Ingersoll-Rand Company)

FIGURE 6. Underground mining at Conda, Idaho, showing the two-speed electric slushing hoist, used for slushing rock and hoisting timbers, set up in a raise manway. The operator is slushing the broken phosphate rock into the south chute of the raise (right), the north chute can be seen at center background and the top of the timber slide at right center.

sub-levels are drifted in both directions from the raises with 30 to 50 feet spacing along the dip of the beds. Overhand stoping is employed in a sequence of slices from each sub-level to the next one above. The stoping progresses from the surface or upper level downward. After each slice is completed it is caved by blasting out the supporting stulls. A plank floor, previously laid on stulls and extending from wall-to-wall along the bottom of the finished sub-level, serves as a mat to hold the overhead gob for the next slice below. The rock is blasted down into the sub-levels and slushed into the raise chutes[11]. Where the hanging-wall is soft and friable, sub-level stoping or underhand slicing, horizontal or inclined at 40 degrees, is

generally used. In any case, heavy timbering is necessary and worked out slices are blasted down as the stoping progresses downward from the surface.

Percussion drills are used in the hard rock found near the Idaho-Wyoming-Utah common border and in the siliceous rock of Montana; stoper or jackhammer feed-leg types of drills are used with one-inch quarter-octagon drill steel and cross bits. In the soft rocks found in the Bloomington Canyon-Georgetown-Conda-Slug Creek areas, jackhammer feed-leg drills with downstroke rotation are used with auger drill steel tipped with V or fishtail shaped bits. The cutting edges of the bits are faced with hard alloy.

Preparation for Market

Western phosphate rock is used for production of ordinary and triple superphosphate analyzing from 18 to 45 per cent citrate soluble P_2O_5, phosphoric acid of 50 to 52 per cent P_2O_5 and for electric furnace production of elemental phosphorus. Small tonnages of rock are used in iron blast furnaces, for direct application to the soil as flour phosphate rock and for sintering with other materials in the production of fertilizers containing one or more of the minor plant food elements. Western phosphate rock is sold as mine run, lump (for blast furnace), crushed, crushed and dried and pulverized. The pulverized rock is furnished in two grades; rock for acidulation is ground to pass 93 to 95 per cent through 100 mesh, direct application or flour rock is ground to pass 90 per cent through 200 mesh.

Crushing

The comparatively coarse grain texture of western phosphate rock makes it particularly amendable to impact crushing. Except where rock is unusually hard and massive, fixed or swinging hammer crushers are in general use for primary and secondary crushing of western phosphate rock. The mine-run rock is screened over vibrating screens to remove fines, then crushed in impact crushers in one or two stages, depending on the hardness of the rock and the size of product desired. If the rock is hard and massive it is sometimes necessary to crush in three stages. The mine-run lumps are first crushed in jaw crushers to approximately 6 inches in size, after which the product is successively reduced to $-1\frac{1}{2}$ inches, and then to final size in heavily lined impact crushers equipped with wide cast alloy hammers. The soft-to-medium hard rock mined in southeastern Idaho is crushed in one stage to $-\frac{3}{8}$ inch with standard or extra heavy equipment. The softer phosphate rock contains from 4 to 8 per cent moisture and during the winter months dried to $-2\frac{1}{2}$ per cent moisture to prevent freezing in transit. The crushed rock is dried in rotating kiln driers, maintained at a temperature of 275°F. The driers are fired by natural gas, coal or oil.

Calcining

Western phosphate rock is characteristically carbonaceous except in shallow surface deposits where oxidation and leaching have occurred. The organic matter is not particularly troublesome in single acidulation processes but it forms sludge in the phosphoric acid solutions produced in double acidulation practice. For the latter use the crushed rock must be calcined before grinding. In order to avoid unburned organic matter in the cores of the larger particles, it is necessary that the rock be crushed to $-\frac{3}{8}$ inch. The rock is calcined at a maximum temperature of 1675°F in wedge-type roasting furnaces, fired by natural gas or oil. The organic content is thereby reduced to approximately 1 per cent.

Grinding

Ball mills were generally used for dry grinding of phosphate rock until the mechanical difficulties of the high-speed type of roller mills were overcome. Now the latter type of machine is coming into favor for this work. The mills are air swept in closed circuit with centrifugal air separators which remove the ground product. Units range in capacity from 5 to 18 tons of rock per hour, ground to a fineness of from 90 to 98 per cent -100 mesh. Damp rock can be dried during the grinding operation by addition of a coal-, oil- or gas-fired furnace to the circuit. Fineness of the grinding is regulated by the rate at which rock is fed to the mill and by adjustment of the vanes which control the centrifugal flow of rock and air within the separator. Uniformity of product, for any given setting, is maintained by automatic adjustment of the rate of feed. The controlling device is actuated by the differences in aerostatic pressure within the circuit. Flour rock has been produced intermittently by several western mills with the above equipment. There has been no firm market for flour rock in the western states. The scant demand for raw pulverized rock for direct application to the soil has come almost entirely from the peat soil areas in Oregon and northern California, where the use of 100-mesh rock has given satisfactory results.

Cost of Production

Prior to World War II western phosphate rock prices had become more or less stabilized on a basis of $3.50 to $4.00 per short ton for mine-run rock of 32 per cent P_2O_5 grade, FOB mine. Pulverized rock, 85 to 93 per cent -100 mesh, sold for $5.00 to $5.50 per short ton, bulk, FOB mill. The subsequent rapid rise in labor and material costs and the development of surface stripping mines, with their attendant problems of shale disposal, temporarily produced a somewhat confused price structure, mine-run rock having been sold at prices varying from $3.86 to $6.00 per ton during

the past two years. During the latter part of 1948 western mine-run rock of 31.5 to 32 per cent grade was fairly stable at $5.00 per short ton; 100 mesh pulverized rock of the same grade sold for $6.25 to $6.50 per short ton, bulk. No representative mining costs can be given at this time because of the wide variations in conditions at the surface and in the underground mines. An approximate range of the principal cost items are given in Table 3.

In examining these cost figures it must be kept in mind that they represent the approximate extremes for each cost item, which has been or

TABLE 3

Surface stripping		
Diamond drilling and engineering...........	$0.20 to $0.30	per ton of ore devel.
Stripping, soil and detrius.................	.10 to .25	per cubic yard
Stripping shales, including stockpiling......	.25 to .40	per cubic yard
Stripping caprock.........................	.30 to 1.00	per cubic yard
Mining phosphate rock, FOB cars..........	.20 to .35	per ton
Depreciation..............................	.30 to .50	per ton
Depletion or royalties.....................	.10 to .50	per ton
General expense, including taxes...........	.40 to .80	per ton
Underground mining		
Crosscuts, drifts and raises................	$0.30 to $0.55	per ton
Stoping...................................	1.00 to 1.60	per ton
Tramming and hoisting.....................	.20 to .70	per ton
Shops, compressed air, power and misc......	.30 to .75	per ton
General expense, including taxes............	.40 to .80	per ton
Depreciation..............................	.15 to .30	per ton
Depletion or royalty, and amortization of development costs........................	.30 to .70	per ton
Crushing..................................	$0.25 to $0.35	per ton
Drying....................................	.15 to .25	per ton
Calcining.................................	.80 to 1.00	per ton
Pulverizing (approx. 90%–100 mesh).........	.75 to 1.15	per ton

might be attained under present operating conditions. Many of the items vary appreciably from month to month in the same mining operation and it is very unlikely that any mining operation enjoys a total cost comprised of a majority of the lower cost items, or that any producer is burdened with all of the higher range figures.

Acknowledgments

Fertilizer Co. for their kindness in furnishing data and illustrations for this chapter.

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8. Phosphates of South Carolina, Kentucky, Arkansas and Virginia

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Whereas, the phosphate deposits of these states (particularly those of South Carolina) have produced substantial tonnages of phosphate rock in the past, none are being exploited at the present time. The cessation of mining operations in most cases has been due to one or more of the following adverse factors: high mining costs, poor yields and the relatively low-grade of the rocks as compared with that produced in Florida, Tennessee and the western states.

Large tonnages of phosphate rock however still remain in some of these states and as mining and metallurgical methods are improved, new processes developed and richer deposits are depleted, it is logical to expect that mining activities in certain abandoned fields will be resumed. Moreover, since some of these deposits are strategically situated to supply local fertilizer demands the saving in shipping charges may offset to some extent the higher mining and milling costs and the lower grade of the product.

SOUTH CAROLINA PHOSPHATE

According to Holmes[10] the nodular phosphates of South Carolina were discovered as early as 1842 in a search for marl or agricultural limestone, but the nature of this rock was not recognized until about eighteen years later. In 1860 Dr. Charles U. Shepard of Charleston made analyses of some of this nodular material and reported the presence of calcium phosphate[5] but the war between the states which began a few years later delayed mining operations.

In 1867, however, Dr. St. Julien Ravenel of South Carolina and Dr. N. A. Pratt of Georgia, both of whom were convinced of the economic importance of these deposits, interested some northern capital and organized the Charleston Mining and Manufacturing Co. The following year (1868) development work was begun and the first shipment of South Carolina phosphate was made in April of that year.

Other companies were soon organized and mining operators proceeded at an accelerated rate. At that time, and until the discovery of the Florida

phosphates, the South Carolina deposits were the largest and most important in the world. The early history and development of the Carolina phosphate industry are fully covered by Chazal[5], Holmes[10], Mappus[13], Shepard[21], and Wyatt[24].

Whereas, there is considerable difference of opinion concerning the exact age and derivation of the South Carolina phosphates it is generally agreed that they belong to the Tertiary Period and according to Rogers[19] are derived from the Edisto phosphatic marl (Miocene) which was enriched in phosphate by leaching out the carbonate of lime and by partial replacement of the carbonate with phosphate.

The phosphate area of South Carolina lies along the coast in a belt which in places is fully 20 miles wide, extending from the Wando River in Charleston County to the Broad River in Beaufort County. The coast region as a whole is but little above tide level and is intersected with numerous creeks, rivers and arms of the sea. The phosphate area therefore not only has excellent rail transportation facilities but large vessels can be loaded close to the mines and the phosphate shipped directly by water either to foreign ports or to Charleston where many fertilizer factories are located.

The South Carolina phosphate deposits were formerly classified under two heads, namely, River Rock and Land Rock. The former was at first most eagerly exploited since it was dredged from the beds of streams and was fairly free from objectionable impurities. This product was washed, picked over and finally dried on ricks of wood. The average grade of the dried product was about 58 per cent tricalcic phosphate (BPL). When a satisfactory method of cleaning the land rock was devised these latter deposits were rapidly developed and the mining of river rock finally abandoned. These types of deposits, however, are composed of the same material, the river rock being merely the land rock washed down and concentrated in beds of streams.

River mining thrived for a number of years, but since it involved the recovery of the mineral from navigable streams that were under control of the state, the industry became involved in litigation that seriously hampered operations. The dredging and auxiliary equipment required was very costly and when the higher grade phosphates of Florida and Tennessee were discovered, competition became very keen. An ill-advised legislature also raised the royalty paid to the state from $1.00 to $2.00 per ton and to make matters worse, a cyclone in 1893 destroyed most of the barges and dredges engaged in mining river rock.

Although some of the equipment was replaced, river rock mining never fully recovered from these blows, and in 1900 production began to fall off rapidly. Nine years later operations ceased entirely.

During the first six years of development the output of land rock exceeded that of river rock. The latter then forged ahead for 5 years, but

from 1878 up to the time that all mining operations ceased, the bulk of South Carolina phosphate was obtained from land mines.

Land rock occurs as boulders, nodules and small pebbles imbedded in a matrix of sand and clay. These nodules or boulders, which range in color from light gray to black, are of medium hardness and are frequently much pitted, the pits being filled with clay or foreign material which must be removed by scrubbing with water in order to obtain a product of sufficiently high grade for acid treatment.

For the first ten years South Carolina land rock was mined almost entirely by hand and the washing of the rock was so imperfect that the grade was poor. Later, however, mining machinery and mechanical washers were installed which made it possible to turn-out a higher grade and more uniform product. The washing process as finally developed was very similar to that employed in the hard-rock phosphate regions of Florida. After thorough washing the rock was dried by firing it on cordwood, a fuel that was plentiful and cheap at that time.

The average grade of land rock after washing and drying was only about 60 per cent tricalcium phosphate (BPL) with a low content of iron and alumina, but a rather high percentage of calcium carbonate.

The South Carolina phosphate beds have an average thickness of only about one foot and hence mining operations were considerably more costly than in the Florida pebble fields where the deposits are in some instances fully 30 feet in thickness. On the other hand, before the advent of flotation the recovery of rock per ton of material handled was higher, and the losses of phosphate entailed in washing the South Carolina rock were not as great as in preparing Florida pebble for the market.

The development of flotation processes, however, made it practical to save the fine particles of phosphate previously lost or discarded in washing and screening Florida rock with the result that the percentage of marketable grades recovered from the matrix has risen sharply and now exceeds that formerly recovered from South Carolina matrix.

In spite of the fact that Florida phosphates were higher grade and more cheaply mined, for many years there was still a demand for South Carolina phosphate in the states as well as by certain foreign consumers who were familiar with its acidulation and had found that it gave a very satisfactory superphosphate. Much of the foreign demand for mineral phosphates is now supplied however from the phosphate deposits of northern Africa.

The peak of production in South Carolina was reached in 1893 when 618,569 tons of phosphate rock were marketed, but from this date the output gradually declined chiefly because of the discovery and development of the higher grade and more cheaply mined phosphate deposits of Florida and Tennessee. In 1921, however, mining operations in South

Carolina ceased entirely and in 1922 only 1,500 tons were marketed from stock piles.

The production of South Carolina phosphate from 1868 until 1912 is given in Table 1.

TABLE 1. PRODUCTION OF MARKETED PHOSPHATE ROCK IN SOUTH CAROLINA, 1867–1912, IN LONG TONS*

Year	Land rock	River rock	Total	Year	Land rock	River rock	Total
Ending May 31				Ending Dec. 31—*Contd.*			
1867	6		6				
1868	12,262		12,262	1890	353,757	110,241	463,998
1869	31,958		31,958	1891	344,978	130,528	475,506
1870	63,252	1,989	65,241	1892	243,653	150,575	394,228
1871	56,533	17,655	74,188	1893	308,435	194,129	502,564
1872	36,258	22,502	58,760	1894	307,305	142,803	450,108
1873	33,426	45,777	79,203	1895	270,560	161,415	431,975
1874	51,624	57,716	109,340	1896	267,072	135,351	402,423
1875	54,821	67,969	122,790	1897	267,380	90,900	358,280
1876	50,566	81,912	132,478	1898	298,610	101,274	399,884
1877	36,431	126,569	163,000	1899	223,949	132,701	356,650
1878	112,622	97,700	210,322	1900	266,186	62,987	329,173
1879	100,779	98,586	199,365	1901	225,189	95,992	321,181
1880	125,601	65,162	190,763	1902	245,243	68,122	313,365
1881	142,192	124,541	266,734	1903	233,540	25,000	258,540
1882	191,305	140,772	332,077	1904	258,806	12,000	270,806
1883	219,202	159,178	378,380	1905	234,676	35,549	270,225
1884	250,297	181,482	431,779	1906	190,180	33,495	223,675
1885	225,913	169,490	395,403	1907	228,354	28,867	257,221
				1908	192,263	33,232	225,495
Ending Dec. 31				1909	201,254	6,700	207,954
1885	149,400	128,389	277,789	1910	179,659	0	179,659
1886	253,484	177,065	430,549	1911	169,156	0	169,156
1887	261,658	218,900	480,558	1912	131,490	0	131,490
1888	290,689	157,878	448,567				
1889	329,543	212,102	541,645	Total	8,721,518	4,105,195	12,826,713

* *U. S. Geol. Survey Mineral Resources,* 1892, p. 782, 1893.

From time to time attempts have been made to revive the South Carolina phosphate industry, but without success. Since the yield of rock per acre is only a fraction of that recovered from the Florida pebble deposits and the BPL content of the product is from 10 to 12 per cent lower, the possibilities of competing with Florida are rather remote.

In 1937 Bennett[1] reported that a thorough investigation had been undertaken to determine the extent of the river deposits and develop economic methods of mining, beneficiation and recovery. The results of this in-

vestigation were said to be highly encouraging for re-establishing a local industry but so far no developments have taken place.

Contrary to general opinion, however, the phosphate deposits of South Carolina are by no means exhausted and the reserves of land rock (60 per cent BPL) have been estimated by the United States Geological Survey[12] at approximately 8,900,000 tons. This is exclusive of the supply of river rock for which there are no reliable figures.

KENTUCKY PHOSPHATE

According to Phalen[18] the phosphatic nature of certain limestones in Kentucky was first recognized in 1877 by Dr. Robert Peter, chemist of the Kentucky Geological Survey. This author described a thin layer of highly phosphatic limestone occurring in the Lower Silurian (Ordovician) near Lexington. The samples collected and analyzed, however, indicated that the phosphate rock was too uncertain in its composition and too irregularly distributed among the poorer limestones to have any great commercial value.

Attention was again called to the presence of phosphate layers at the top of the so-called Trenton Limestone by A. M. Miller[14] as early as 1896, and again in 1904 when this geologist was engaged in some field work in Jessamine, Woodford and Franklin Counties. It was not until 1905, however, that interest began to be evinced in Kentucky phosphate and actual development work was only begun five or six years later.

Between 1912 and 1915 several surveys were made and reports issued [8, 9, 15, 18, 22] on the Kentucky phosphate deposits which caused considerable activity in this field and prospecting work was carried on at various points in Fayette, Woodford, Scott and Jessamine Counties. So far, however, the deposits have proved to be somewhat spotty and no workable beds comparing in size with those of Florida and Tennessee have been discovered. Only in Woodford County near Wallace and Midway has any appreciable tonnage been mined.

The Kentucky phosphate region forms part of the great Cincinnati "geanticline" extending from Nashville, Tennessee, in a northeasterly direction through Lexington County, almost to Cincinnati. South of this city it divides into two broad domes, one culminating near Nashville and the other in Jessamine County, Kentucky. The latter is known as the Jessamine Dome. All of the exposed rocks of these regions are of sedimentary origin and the arching of the strata took place so gradually that the horizontal position of the rocks is but little altered.

The following description of the geological occurrence and origin of the Kentucky phosphate is abstracted from the report of W. C. Phalen[18].

"The country rocks associated with the phosphate rock deposits are all

limestones of different lithology and degrees of purity. They are all of marine origin and belong to the middle part of the Ordovician system; their total thickness is approximately 330 feet.

"The rock of Central Kentucky belongs entirely in a class known as brown phosphate, first so-called in middle Tennessee. It occurs as a distinctly laminated residual deposit, also as filling solution cavities or pockets in a more or less phosphatic limestone. The rock itself occurs in porous or loosely coherent plates, varying in thickness from the very thinnest up to those several inches thick. Usually the plates are separated from each other by layers of loosely cemented or porous material consisting of phosphate rock in a fine state of division, mixed with more or less clay. There is also another form of brown rock, known as phosphate sand, some of which is very rich in calcium phosphate."

While individual samples of Kentucky phosphate have analyzed as

TABLE 2. COMPOSITION OF DIFFERENT TYPES OF KENTUCKY PHOSPHATE

Sample No.	Location	Description	Analyses			
			Si_2O	$Fe_2O_2Al_2O_2$	P_2O_5	$Ca_2(PO_4)_2$
200	Near Midway, Ky.	Light yellow, soft	24.29	17.18	21.34	46.71
201	Near Midway, Ky.	Dark brown, close grained plates	2.63	2.75	35.71	78.17
202	Near Midway, Ky.	Dark brown, porous hard	4.88	3.67	34.00	74.43

high as 78 per cent tricalcium phosphate, the average grade of rock is probably considerably below that of the brown rock phosphate of Tennessee. Phalen[18] gives the thickness of the phosphate beds as well as the BPL content of samples collected from various localities throughout the phosphate area. His data show wide variations both with respect to the thickness and grade of the rock.

Analyses made by this writer[22] of a number of different types of Kentucky phosphates are given in Table 2.

In 1912 several farms near Wallace were leased by the Central Kentucky Phosphate Company with a view to developing the deposits in that area. The company was later taken over by the United Phosphate and Chemical Company and a plant erected in 1919 to mine and prepare the rock for market. Operations were continued intermittently for a number of years but the methods employed were rather crude. The overburden was first removed by scrapers and the exposed rock then mined with pick and shovel. The beds in this area ranged from 3 to 5 feet in thickness, but much of the material was in finely divided or distintegrated form. The rock was loaded into cars, hauled to the plant and dried in a rotary kiln.

The dried phosphate was then screened and all material coarser than one-half inch marketed as high-grade rock. The minus one-half inch material (60 per cent BPL) was then crushed, finely ground and sold for direct application to the soil.

This plant was not equipped with a washer or any other means for raising the grade of the product and in 1926 the mine and plant were shut down. No production of phosphate rock has been reported from Kentucky since that date, but during the seven years of operation over 93,000 tons were mined. The average grade of this rock was probably considerably under 70 per cent BPL, but this was due in part, at least, to the lack of proper beneficiation equipment.

According to Phalen[17] the reserves of phosphate rock in Kentucky are in the neighborhood of 863,000 long tons, which means that not more than about 11 per cent of the rock has been mined.

ARKANSAS PHOSPHATE

At present these phosphate deposits are not generally regarded as of much economic importance since compared with the product of Florida, Tennessee, the western States, and even South Carolina, the rock is of a low grade.

The deposits, however, are well situated to supply the growing demand for fertilizers west of the Mississippi River and though much of the material is too low in P_2O_5 and too high in iron to make it desirable for the manufacture of superhosphate by the sulfuric acid process, the development of thermal methods of producing phosphoric acid and available phosphates may result in the renewal of mining activity in these fields.

While mention is made of the occurrence of phosphate in a number of localities in Searcy, Izard, Stone, Marion, Baxter and Boone Counties, the rock has been developed only in the northwestern part of Independence County along Lafferty Creek north and west of the White River and about 10 miles from Batesville. The phosphatic nature of these beds was first recognized by Branner[2] in 1895, and exploitation was begun about five years later.

The deposits were formerly considered of Devonian age[3, 4] but more recent investigations have shown them to be older[16, 22]. The rocks of the phosphate horizon vary considerably in character, but there are always bands of shale occurring among the phosphate strata. Manganese ore is also closely associated with phosphate in many places, much of the rock being stained by this substance[16].

The phosphate in the developed area occurs in two strata—one directly overlying the other. The first, or upper layer, is from $3\frac{1}{2}$ to 6 feet in thickness and consists of a hard massive rock made up of rounded fragments of

organic debris closely cemented together. It varies in color from light gray to brownish black, the color largely depending on the quantities of iron and manganese present. This bed averages from 55 to 60 per cent bone phosphate of lime. Directly under this bed lies a second stratum of phosphate rock from 2 to 4 feet in thickness, which closely resembles that just described. It is, however, less oolitic and contains appreciably less P_2O_5. The average grade of this second stratum is from 30 to 40 per cent bone phosphate of lime and therefore during mining operations it was separated from the upper stratum and thrown away as unmarketable rock.

TABLE 3. ANALYSES AND DESCRIPTION OF PHOSPHATE STRATA FROM TWO DIFFERENT LOCALITIES IN ARKANSAS

Sample	Location	Thickness of Strate	Description	Analyses	
				P_2O_5	$Ca_2(PO_4)_2$
	Phosphate, 12 miles northwest of Batesville	2' 6"	Ferriginous Limestone (roof)	Trace 5.82	..... 12.72
93		6"	Green shale	28.85	63.05
89		4' 0"	Hard, gray, nodular	14.16	30.94
91		2' 0"	Hard, gray, less nodular		
97	1¾ miles north of Phosphate	1' 6"	Ferriginous phosphate	19.60	42.94
94		6"	Thin bedded slate (not sampled)	.....	.....
96		3' 0"	Hard, gray, oolitic phosphate	22.96	50.18
95		1' 0"	Hard, gray, oolitic phosphate	10.01	21.87
98		Undetermined	Ferriginous shale	7.53	16.45

In Table 3 are given the analyses and descriptions of the successive strata of phosphate rock sampled by the writer at two different places.

Arkansas phosphate was mined in the same way as the blue rock phosphate of Tennessee, by first stripping around the face of the hill untill the overburden became too heavy to be profitably removed, and then running drifts into the hill's side. As these tunnels are driven deeper into the hills comparatively little timbering is required since the stratum of unweathered limestone and shale overlying the phosphate beds form a fairly substantial roof.

For a number of years substantial tonnages of phosphate rock were produced from these deposits and shipped to Little Rock, Arkansas, where it was manufactured into low-grade superphosphate. The development of the higher grade phosphates in Tennessee, however, rendered the mining of

Arkansas rock unprofitable and in 1912 operations ceased entirely. According to Branner[3] the total output during this period amounted to 31,472 tons.

The Arkansas phosphate deposits are by no means exhausted and Mansfield[12] estimated the remaining reserves at 20,000,000 tons. However, there appears little likelihood that mining operations will be resumed unless some favorable factors develop which will make it practicable to utilize the rock direct or beneficiate it at low cost so it can be used in established methods of producing phosphoric acid and available phosphates.

Virginia Phosphates

In Nelson and Amherst Counties of west-central Virginia large dikelike bodies of ore occur consisting of a mixture of apatite and ilmenite and apatite and rutile. For many years little importance was attached to these deposits although a considerable tonnage of rutile was extracted in the area near Roseland, Nelson County, Virginia.

Watson and Taber[23], in describing these deposits and reporting on the geology of the region, concluded that Nelsonite is an igneous rock, but Ross[20] later claimed that it is the result of hydrothermal replacement in a post-magmatic stage. Still later, Davidson *et al.*[6] described these deposits as irregular apatite-ilmenite dikes intruded into a once closely related anorthosite, and subsequently altered by hydrothermal agencies. Watson named this peculiar ore Nelsonite because it was first found in Nelson County.

Unweathered nelsonite is a dark, granular rather hard rock, but the weathered material has some tendency to crumble and the individual grains of light colored apatite are more in evidence. Ilmenite, is the predominating mineral, consituting about 45 per cent of the weight of the ore, whereas, the apatite content is in the neighborhood of 20 per cent. The ratio of ilmenite to apatite appears to be fairly constant.

When processes for the manufacture of titanium pigments from ilmenite were developed, the nelsonite deposits began to attract considerable interest, and investigations were undertaken with a view to separating the two industrial minerals contained therein. From a technical standpoint this problem was rather successfully solved by applying standard ore dressing methods.

Exploitation of the deposits at Piney River was undertaken in 1937 by the Southern Mineral Products Corp. (a subsidiary of the Vanadium Corp.), and the concentrates obtained were sold to an adjacent plant of the Virginia Chemical Corp. for processing. This plant produced phosphoric acid and monocalcium phosphate from the apatite for a number of years, but in 1943 their manufacture was discontinued and a plant for producing de-

fluorinated phosphate was constructed. After several changes in owner-
ship the property passed into the Calco Chemical Company (subsidiary of
the American Cyanamid Co.).

The following description of the methods employed in mining and milling
the rock and separating the two marketable minerals is taken from a report
by Ferney[7].

"The ore is broken by electrically exploded dynamite and trammed to
the mill where it is weighed and broken through the grizzly.

"Ore that has passed the grizzly is conveyed to a jaw crusher, further
reduced and passed on to the mill crude-ore storage bin. The sample is
assayed for moisture, TiO_2 and P_2O_5 content.

"Ore from the crude-ore storage bin is conveyed to the mill where it is
fed into a rod mill with a certain quantity of water and there subjected
to a mild grind or severe scrubbing which is sufficient to break the grains

TABLE 4. ANALYSIS OF APATITE CONCENTRATE DERIVED FROM NELSONITE

	(%)
P_2O_5	40.88
$Ca_3(PO_4)_2$ (equivalent)	89.32
CaO	63.94
Fe_2O_3	0.54
Al_2O_3	0.58
F	3.61
TiO_2	.05
H_2O	.06
Loss on ignition	.08

of mineral apart without grinding them to any extent. The resultant pulp
. . . is pumped to a vibrating screen where it is sized. Oversize from the
screen is returned to the rod mill for further grinding and the undersize is
carried by gravity to the classifiers.

"Much of the material in the pulp that passes through the screen is
very fine and would interfere with the magnetic separation of coarser
particles. The function of the classifiers is to remove this fine material.
The remaining coarse material or sand is washed before leaving the classi-
fier and then fed into a rotary dryer from which it is discharged as a hot,
free-running sand.

"The hot discharge from the dryer is next passed over a cooler and then
conveyed to a storage bin. Sand from the storage bin is fed by gravity to
the magnetic separator which is of the induction three roll type and more
or less designed for this particular process. The separator consists of a
series of rolls set in the path taken by the magnetic flux produced by an
electromagnet. . . .

"By passing the dry sand over the rolls of this separation unit it may be
separated into three different products: (1) a black, highly magnetic ilmen-

ite concentrate removed by weakly magnetic rolls; (2) a brown micaceous, weakly magnetic tailing product removed by the strongly magnetic rolls; and (3) a granular, nonmagnetic apatite concentrate which remains when all the magnetic materials have been removed."

Ferney[7], in Table 4 gives the following analyses of the apatite separated from Nelsonite by the method outlined above.

It was claimed that this apatite, on account of its low content of organic matter and oxides of iron and aluminum, yielded phosphoric acid of such high quality that little purification was necessary. For some years the acid produced therefrom was used in manufacturing food-grade monocalcium phosphate, but apparently this proved unprofitable as both the mine and plant were shut down in 1948[11].

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9. Phosphates of Foreign Countries

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Although the United States in 1948 produced nearly one-half of the world's output of phosphate rock, this has been true only since World War II. However, since the end of the war, the foreign phosphate rock producers have been doing their best to recover their production capacity and resume their prewar position of producing about two-thirds of the world's consumption.

The economies of the countries in Europe and Asia need phosphate rock badly, and if they are to recover, production from the foreign deposits must increase materially. Therefore, it is possible that their production will return to the two-thirds of world's supply as before the war.

NORTH AFRICA

Morocco, Algeria and Tunisia are the three countries comprising this sizeable French controlled area in northwestern Africa with 535 miles of Atlantic shoreline and 1,130 miles along the Mediterranean. The population of French North Africa before the war was said to be about 16 million, of which 90 per cent were native moslems, the balance mostly French, except in Tunisia where there are almost as many Italians as French.

Morocco is to the west on the Atlantic Coast with very much smaller Spanish Morocco to its north, leaving it only about 10 miles of shoreline on the Mediterranean. It is a French protectorate whose political head is a Sultan and it is about the size of California.

Algeria is in the middle, and about three times the size of Texas, because it extends far to the south into the Sahara Desert. Most of its population lives near its 640 miles of Mediterranean coast. Politically, Algeria is the equivalent of a state of France and sends its elected representatives to the Chamber of Deputies in Paris.

Tunisia to the east is about the size of Alabama with a northern and eastern coastline on the Mediterranean for about 480 miles. It is a French protectorate presumably headed by a Bey.

The phosphate rock deposits of these three countries are really in two areas, one of which is entirely within Morocco and the other on either side of the border between Algeria and Tunisia. These deposits are secondary

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phosphorites in beds between other sediments such as limestones, sandstones and shales. With a few exceptions they are mined by underground methods.

Because of the increasing demand for phosphates in Europe where intense agriculture must be carried out to feed its large population, production in Algeria commenced in 1893, followed by Tunisia in 1897. It was not until 1921 that Morocco started, and by the middle 1920's production of phosphate rock in French North Africa exceeded that of the United States. This production rate continued until World War II, when phosphate production fell to low levels practically everywhere except in the United States. This was mainly due to the difficulties of water transportation caused by the war.

Morocco Deposits[1, 7, 11]

Between the Atlas Mountains and the Atlantic Coast to the west, these deposits traverse an area in the rolling plain for a distance of about 200 miles. They are in Eocene limestones, shales and sandstones, usually only moderately folded. The phosphorite mined is an altered limestone of marine origin, formed in beds 6 to 10 feet thick. There are other phosphorite beds but they are less attractive from a mining viewpoint.

At Khouribga, about 125 miles by railroad to the southeast of the port of Casablanca, is located the larger of the two operating mines in Morocco and that which produces the higher grade phosphate, usually running about 75 per cent BPL.

This deposit has been opened by three main adits on the down slope of the phosphate bed, approximately 5 to 10 per cent grade, traversing the bed to the underground water level, a distance of from 3,000 to 8,000 feet as measured along the incline. Mining of the 10 foot bed of phosphate is accomplished by the room-and-pillar method. The pillars are mined later by retreating methods similar to those used for long-walls.

In 1938 it was said that it would be many years before phosphate rock above the underground water level would be exhausted at the production rate then prevailing. For this reason no plans were made for mining the continuation of the bed below the water level.

This phosphate bed is relatively soft and requires a minimum of drilling and blasting. The broken rock was loaded into small mine cars and hand-trammed to the main haulage adits where the cars were attached to an endless cable and hauled to the surface through the three main haulage adits and to a drying plant located nearby.

At this drying plant the large lumps were crushed and passed to trommels where the oversize (wall-rock) was removed, the balance going to wet-rock storage bins having a capacity of about 75,000 metric tons. From these

bins the wet-rock was mechanically fed to cylindrical driers which, in turn, delivered the dry-rock (minus 3 per cent moisture) to belt conveyors leading to hopper-bottom dry-rock bins. These bins fed the dry-rock to gondola cars by gravity for transportation over an electric railroad of one-meter gauge to the main storage bins at the port of Casablanca.

The summer is very dry in Morocco for about four months when the Socorro winds blow over the Ural Mountains from the Sahara Desert. During this period the wet-rock is not passed through mechanical driers; instead it is spread out to a thickness of about a foot on specially prepared level areas near the drying plant. These areas are served by three types of Diesel machines; one for taking the phosphate from the cars and spreading it evenly, another to rake over the beds of phosphate to hasten the drying, and a third to pick up the sun-dried phosphate (5 per cent moisture) and load it into cars which are hauled directly to the bins at Casablanca.

The pier at Casablanca was especially designed for storing phosphate rock and loading it into ocean vessels. The storage bins have a capacity of about 75,000 tons. By means of an especially elaborate belt conveyor system the bins are loaded from the railroad cars and the phosphate is loaded into the boats at the rate of about 1,000 metric tons per hour.

Phosphate mines in Morocco are owned by the Office Cherifien des Phosphates. The capital investment was supplied by the French govern-ment which took as security an issue of first mortgage bonds in "OCP", the common stock going to the Moroccan government. Practically all of the personnel in management in Morocco is French and report to the main office in Paris.

Khouribga was the first phosphate rock mine developed in Morocco and was put in operation in 1925. Its product is known in the trade as "Morocco phosphate" and is sold "tel quel", guaranteed to grade not less than 73 per cent BPL, though shipments usually run close to 75 per cent BPL. When Khouribga came into operation demand for phosphates in Europe was rapidly increasing. Because of the shorter ocean haul, cheap labor, and the high grade of its phosphate rock, it succeeded in taking away the greater part of the exports from the Florida pebble field to northern Europe. In 1939 Khouribga shipped over a million tons of phosphate rock from Casablanca. Loading facilities at Casablanca are shown in Figure 4.

The other phosphate rock mine in Morocco, located about 130 miles southwest of Khouribga is known as the Louis Gentil mine. Development work commenced about 1930 and shipments began in 1935 through the port of Safi on the Atlantic Coast, about 140 miles south of Casablanca.

Louis Gentil was opened up similarly to Khouribga but with only one main haulage adit. The phosphorite bed is of about the same thickness and the same method of mining is used. The phosphate is hauled out of the

adit by cars attached to an endless cableway which delivers them to a small crushing plant. It is hand-picked on travelling steel belts for the removal of chert and wall rock, then delivered to storage piles. From this point a
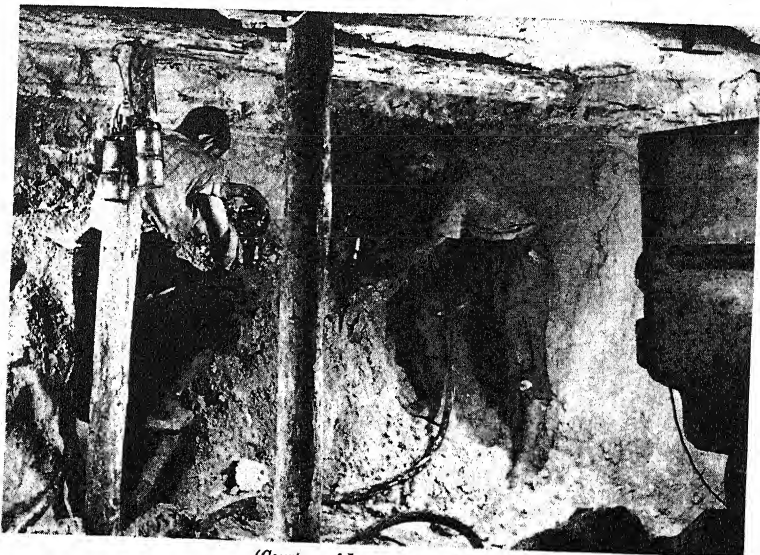
(*Courtesy of International Minerals and Chemical Corporation, Ltd.*)
FIGURE 1. Mining Moroccan phosphate with pneumatic drills.

(*Courtesy of International Minerals and Chemical Corporation, Ltd.*)
FIGURE 2. Method of sun-drying Moroccan phosphate.

(Courtesy of International Minerals and Chemical Corporation, Ltd.)
FIGURE 3. Drying plant of the Khouribga Mine.
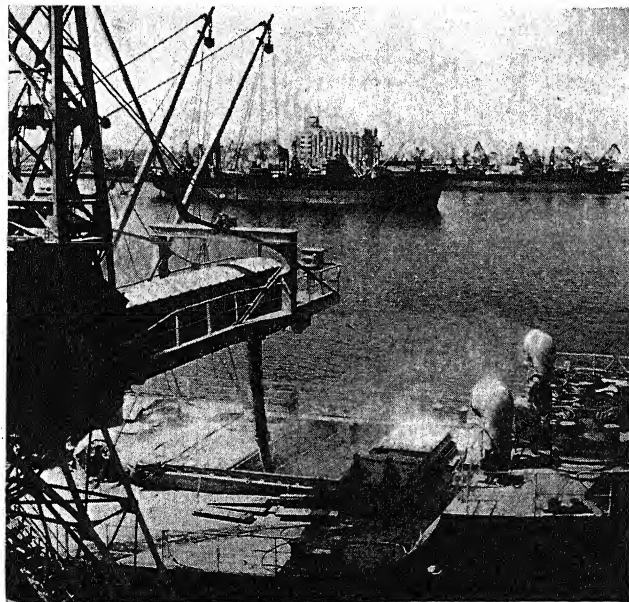
(Courtesy of International Minerals and Chemical Corporation, Ltd.)
FIGURE 4. Loading Moroccan phosphate for shipment at the Port of Casablanca.

belt-bucket excavator delivers the phosphate to an aerial tramway which carries it about $2\frac{1}{2}$ miles over rolling country to the drying plant at Louis Gentil village. This drying plant is much smaller than the one at Khourigba, but very similar. From the dry-rock storage bins the phosphate is hauled by rail about 35 miles to the port of Safi. Here a similar but smaller layout for storage and boat loading is installed on a pier. Louis Gentil phosphate is known in the trade as "Safi phosphate" and grades about 70 per cent BPL.

During World War II, with Germany occupying Morocco, shipments from these two Moroccan mines dropped from 1,703,000 metric tons in 1939 to a low of 511,500 tons in 1941. Since then shipments have gradually increased, especially since 1943, to 4,038,000 tons in 1950[10a]. During the German occupation most of the phosphate was shipped to Germany and Italy.

Algeria-Tunisia Field[7, 11]

In sediments of lower Eocene age, on either side of the boundary line between the province of Algeria and the regency of Tunisia, are several deposits of phosphorite. These deposits are very similar to those in Morocco. Operations were started as early as 1893 in Algeria and about four years later in Tunisia. As these mines were operating some twenty years before the Moroccan mines they were the principal source of phosphates for Europe during the early part of the century. The deposits are well located, especially those in Tunisia, for shipment by boat across the Mediterranean to the southeastern European countries and to the Near East.

Early production of phosphate rock in Algeria was greatly hampered by unscientific methods, labor difficulties, French legislation and American competition. The operators of the Tunisian deposits profited by the mistakes of their Algerian predecessors and soon were the principal suppliers of the European market. In 1949 Tunisia produced more than twice as much phosphate rock as did Algeria, but together their production was less than that of Morocco.

As the deposits are very similar to those of Morocco the mining operations are also very much the same. With a few exceptions, the mines are opened by one or more haulage adits from the surface outcrop following the bed of phosphorite. Practically the same underground mining methods are used. The exceptions are some open pit mines in Algeria. All mines are operated by private companies.

The important producer in Algeria is the Cie. des Phosphates de Constantine, which has been operating since 1893 at Djbel Kouif, about 13 miles northeast of Tebessa, close to the Tunisian boundary line. Phosphate from this mine was shipped through the port of Bone in northeastern

Algeria on the Mediterranean. The many years of operations at annual productions of from 400,000 to 800,000 metric tons have about exhausted this deposit. In recent years this same company acquired a concession to develop other large deposits located about 50 miles south of Tebessa that can be mined by open-pit methods. These new deposits are expected to supplant those at Djebel Kouif as the latter are mined out. A railroad will be built from Djebel Onk, where this mine is located, to Tabessa to connect with the existing railroad to the port of Bone.

Another open-pit mine is operated by Cie. M'Zaita near the town of Setif. This phosphate is hard and breaks in quite large sizes. It is sold principally to the steel industry in Europe, shipments being made through the port of Bougie.

Production from Algeria in 1939 was about 500,000 metric tons but during the war years, with German occupation and shipping difficulties, production dropped very low. After the Allies took over, shipments began to increase and by 1947 Algeria had recovered with shipments of 713,000 metric tons. Increase in the cost of labor is said to be holding back further developments in Algeria.

Most of the Tunisian production of phosphate comes from the Gafsa-Metlaoui-Redeyef area. These mines ship through the ports of Sousse and Sfax, about 175 and 150 miles east of the mines. There are some smaller mines in the northern area of Tunisia which ship through Tunis.

For many years the largest phosphate rock producer in the world has been the Cie. des Phosphates et du Chemin de Fer de Gafsa which also owns the rail lines to Sfax and Sousse. In normal times Gafsa produces more than a million tons annually from its mines near Rodeyef, Metlaoui and Gafsa. However, with the increasing demand for phosphate rock in the United States since the end of the war, the probable world's largest producer is the International Minerals & Chemical Corporation operating in the Florida pebble, Tennessee and western fields of the United States.

Other companies operating in Tunisia are known in the industry as Tunisiens, M'Dilla, Dyr, and St. Gobain.

In 1930, just before the world-wide depression, Tunisian production reached a peak of 3,226,000 metric tons. The war, with its German occupation, reduced this to a fraction. No doubt Tunisian production will return some day to the 1930 figure or exceed it, if and when real peace returns to Europe with its normal economy.

Production from the Algerian-Tunisian field totalled about 2,128,000 metric tons in 1939, only 1,006,000 tons in 1945, recovering to 2,534,301 tons in 1948.

During these same years the total production from French North Africa was 3,831,000 metric tons in 1939, about the same as that of the United

States; 2,641,000 tons in 1945, less than half; and 5,760,627 tons in 1948, or a little less than two-thirds of the United States production during that
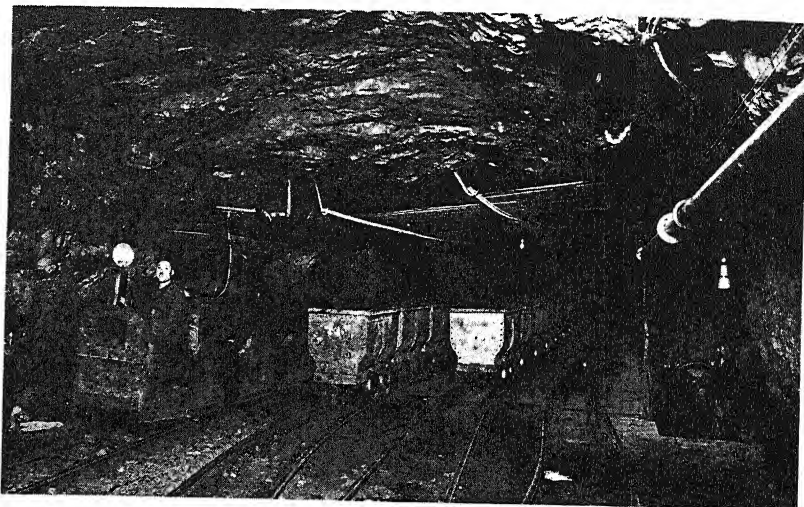
FIGURE 5. Underground phosphate mine in Algeria. Phosphate cars being hauled out of main gallery.
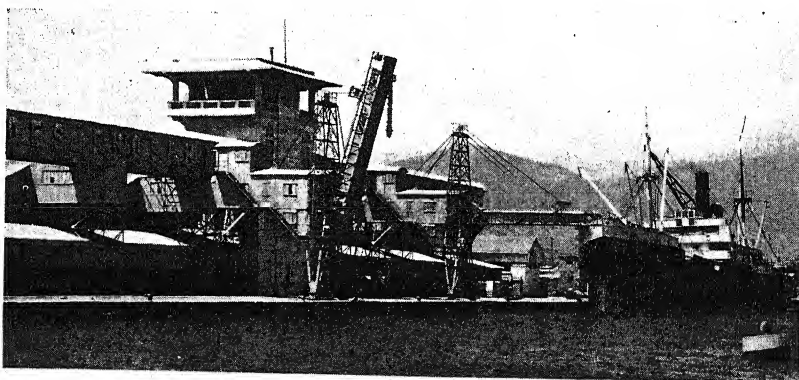
FIGURE 6. Phosphate loading plant at Bona, Algeria.

year. In 1948 the Florida pebble field alone produced more phosphate rock than did the whole of French North Africa. Figures 5 and 6 show the mining and loading of Algerian Phosphates.

Egypt[7, 11]

Phosphate rock production commenced in Egypt in 1908. Today there are two mines producing, although their shipments have never been very large. Most of the Egyptian phosphate is exported. One of the mines is operated by an English company at Safaga, about 280 miles southeast of Cairo and about 18 miles west of the Red Sea. An Italian company operates the other mine at Kosseir to the south of Safaga.

Both of these deposits are phosphorites in Cretaceous sediments and are similar to the Tunisian deposits. Mining at Safaga has been an open-pit operation (strip mining) along the outcrop of the phosphorite bed, removing the hanging-wall as overburden to a depth that the cost of mining will warrant. At Kosseir the mining is underground using the room-and-pillar method. The grade of Egyptian phosphate usually ranges between 66 to 68 per cent BPL. The rock is higher in carbonates than most phosphates.

The bulk of the Egyptian phosphate produced in years prior to the war was shipped to Japan from ports on the Red Sea. The war made ocean shipments difficult and in 1941 the output dropped to 112,000 metric tons as compared to 548,000 tons in 1939. Since World War II Egypt's production has recovered somewhat amounting to 377,000 tons in 1948 and 350,000 tons in 1949.

PHOSPHATES OF EUROPE

At one time Belgium, England, and France produced a considerable tonnage of low-grade phosphate rock which was depended upon to meet the agricultural demands of those countries for soluble phosphate fertilizers.

While these phosphate deposits are not yet entirely exhausted the discovery of the vast fields of higher grade and more cheaply mined phosphates in the United States soon caused mining operations in these countries to decline, and since the development of the immense phosphate deposits of Northern Africa and later those of Russia, the output of French and Belgium phosphates has almost ceased.

With the exception of Belgium, these countries own or control extensive and valuable phosphate areas in Africa and on certain islands in the Pacific and Indian Oceans. Next to the United States and North Africa, however, the phosphate deposits of Russia are the most important from the standpoint of production and reserves.

Belgium

The principal phosphate region in Belgium is situated at Ciply and Mesvin, near Mons. These phosphates occur either as nodules imbedded in a matrix of clay or as beds of phosphatic chalk in Tertiary and Cretaceous strata. The grade of rock now available averages only from 40 to 45 per

cent tricalcium phosphate and contains such a large proportion of acid-consuming impurities that it is uneconomical to use alone for the manufacture of superphosphate. Accordingly, the small tonnage mined is mixed with richer phosphates from other sources in order to give available or water-soluble phosphates of marketable grade.

England

Phosphates in the form of coprolites occur over widely scattered areas in the British Isles, but the rock is of such a low grade that it now has but little commercial significance.

The most productive deposits have been those in the Cambridge upper Green Sand, where the beds consist of dark brown or black nodules from 8 to 12 inches thick, and from a bed 12 to 18 inches thick of similar material in Suffolk.

The average grade of the English coprolites is below 50 per cent tricalcium phosphate and the rock contains such a high percentage of iron that it is impracticable to use it for the manufacture of superphosphate unless it is blended with a large proportion of high-grade phosphate from other sources. As in the case of Belgium the exploitation of these coprolite deposits is no longer profitable and production has practically ceased.

France

Low-grade phosphates occur in the Departments of Aisne, Ardennes, Meuse, Oise, Pas de Calais and Somme. The rock is of Cretaceous age and occurs in the form of phosphatic chalk and as narrow bands from 2 to 10 inches thick in Cretaceous Green Sand.

The rock ranges in grade from 45 to 65 per cent tricalcium phosphate and while at one time of considerable importance from an agricultural standpoint is now unable to compete with the phosphates of the United States and Northern Africa. Mining operations, if any, are conducted on a very limited scale—the rock being mixed with higher grade phosphates from other sources and manufactured into superphosphate.

During both World Wars practically all of the phosphate area of France was in German hands, and it is doubtful if any appreciable tonnage was produced.

Germany

No large deposits of phosphate rock of economic importance have been found in Germany, although it was reported that low-grade phosphates were discovered in the vicinity of Neurenburg in 1918. Some phosphorite also occurs in Nassau in the Lahn River basin. Limited tonnages were produced from the latter deposits during World War I and just prior to

World War II but the beds are not only of a low grade but so pockety in nature that they cannot be economically mined in competion with the extensive and high-grade deposits in the United States, Africa and Russia.

Spain

Two deposits of phosphate have been reported in the province of Estremadura, Spain. One occurs in limestone formations and the other is a concretionary variety of apatite. These deposits have been mined since 1865 but production has fallen off markedly since the extensive exploitation of North Africa phosphates. In 1949 the output from Spain was reported to be about 23,000 metric tons.

Sweden and Norway

Apatite occurs in Norway and Sweden but the rock is associated with other minerals and requires hand-picking or beneficiation to render it suitable for the manufacture of superphosphate. Moreover the deposits are not sufficiently large or extensive to permit exploitation in competition with those of the United States, North Africa and the Soviet Union. The apatite in northern Sweden is associated with iron ore, from which it is separated by flotation. During the war a plant was said to have produced about 25,000 tons of apatite per year, but it is doubtful if these deposits can be worked at a profit under normal conditions.

Russia[1, 8]

Russia's deposits of phosphate were first mined in 1885. Many deposits of phosphorite west of the Ural Mountains have been mined from time to time, notably near Podolio and Bessarabia. Superphosphate has been made for many years from Podolio phosphorites. The Kostroma and Viatka phosphorites produce superphosphate containing approximately 12 per cent P_2O_5. Low-grade phosphorites at Smolensk, Koursk, Voronech, Saratoff, Simbirsk and Voleyda have been finely ground for direct application to the soil.

About 1930, on the Kola peninsula, not far from Murmansk, a huge igneous deposit of apatite was discovered in the U. S. S. R. and since then has been developed into one of the world's large sources of phosphate rock. This deposit forms a mountain of a mixture of various minerals, such as nepheline, aegirite, titano-magnetite, titanite and apatite.

The deposit has been opened by driving a large haulage tunnel capable of accommodating complete trains of ore cars of outside railroad gauge. From this main tunnel about 20 miles of smaller tunnels have been driven and equipped with electric haulage.

At the town of Kirovsk, not far from the mine entrance, a large concen-

trating plant has been built equipped with crushers, grinding mills, and the necessary flotation equipment to separate the apatite from the other minerals. The major part of the mine production is treated by flotation and yields a very high-grade apatite concentrate up to 88 per cent BPL. It is said that titanite is also recovered by selective flotation for the production of titanium compounds. That part of the mine production which is not concentrated is shipped direct to metallurgical plants. The annual output of crude and concentrates is estimated at more than two million tons, but there are no accurate production data available.

Murmansk is now connected by rail with Leningrad and other cities of European Russia. As Murmansk is an open port practically all year round, in spite of being within the Arctic Circle, probably most of the Kola phosphate is shipped by ocean vessels. During the 1930's small tonnages of Kola phosphate were imported into the United States.

Apatite is not always competitive with phosphorite on an equal basis, due to its lack of porosity. It is a crystalline mineral and therefore solid, whereas phosphorite is rather porous, even appearing to be dry when actually containing as much as 5 per cent moisture in its very fine pores. When apatite grains are treated with sulfuric acid in the superphosphate process, they are attacked only on the surface, whereas the phosphorite particles absorb the acid within their pores which have an area many times that of the surface of the particles. Apatite requires about three times as long as phosphorite for the chemical reactions to be completed.

There are some phosphate rock deposits in Asiatic Russia. One of these is just east of the Ural Mountains near Ugolny in about latitude N 60°. Another is located about 160 miles southwest of Balkhash on the Golodnaya Steppe near the western end of Lake Balkhash. There are no authoritative figures on Russia's production of phosphate rock but the output in 1947 was estimated at 2,500,000 metric tons.

ISLAND DEPOSITS

In the Pacific and Indian Oceans and in the Caribbean Sea are found many deposits of phosphorites on small islands. Most of these islands are of volcanic origin, formed by the eruption of basic lava quickly cooled. The part of the eruptive cone above sea level gradually eroded away. Then came the zoophytes, organisms that deposit calcium carbonate (coral) on the rocks just under sea level and deeper. Coral was then deposited by these micronisms as a collar around or as a cover over the island. By dropping of the ocean level, or by further volcanic disturbance, some of these islands were raised. Still later there came colonies of marine birds and these birds used such coral islands as homes, probably for centuries, and large deposits of guano (excreta) accumulated. Rain water dissolved the

soluble constituents in the guano and the phosphate solution was fixed by the coral, eventually changing the calcium carbonate into tricalcium phosphate.

When there was no intermixture of detritus from the erosion of the basic lava, the resultant grade of phosphorite was very high, usually over 80 per cent BPL. On some islands where the coral was in the form of pinnacles, much lava detritus, now resembling soil, is mixed with the phosphate, sometimes greatly diluting it with iron and aluminum compounds, resulting in a phosphate sand containing as high as 35 per cent iron and alumina and only 35 to 40 per cent tricalcium phosphate. Such phosphate can be used only for direct application to the soil.

Depending on the type of island deposit, mining is carried on by quarrying, by dredging, and by post-hole digging of the phosphate in holes in the coral.

Japan's Mandated Islands

Japan carried on mining operations on many of her mandated islands received from Germany after the first World War, such as Fais, Peleliu, Angaur, Sonsorol, Tobe, of the Caroline group; Rota, Saipan, Tinain, of the Marianas group; Okina Daito and Kita Daito, of the Ryukyu group; Ebon of the Marshall group; and many other small islands that produced unimportant tonnages.

In 1945, when Japan surrendered to the Allies, these islands had stock piles of mined wet-rock ready to be dried and shipped amounting to 258,000 tons. Unmined reserves on these islands in 1946 were estimated at 2,760,000 tons. Of these reserves Kita Daito had about 1,400,000 tons, Angaur 800,000 tons, and Fais 200,000 tons.

In 1933 these islands produced 98,718 tons. Shipments rose to a maximum of 322,236 tons in 1939 and then gradually fell off to 171,000 tons in 1943, and ceased entirely after shipping about 36,000 tons in 1944. Even at the peak of production these islands supplied only about one-third of the phosphate rock required by Japan for its very intensive agriculture.

Because of the urgent need of phosphates in Japan, General MacArthur, late in 1945, asked for shipments of rock from the United States, and the resumption of production from these islands which at that time were under control of the United States Navy. The Japanese had efficient drying plants and equipment on four of these islands—Angaur, Fais, Rota and Kita Daito—but they had been either destroyed or badly damaged as the Pacific front advanced from Guam. However, the Navy had phosphate production of wet-rock started by June 1946 and loaded the first cargo from Angaur island in August of that same year. In 1947 about 140,000 tons of Angaur phosphate had been shipped to Japan. Upon completion of repairs to plants

and loading piers annual shipments of dry-rock were expected to increase materially. However the relatively limited reserves on these islands will not last many years.

Before the war Japan consumed over 800,000 tons of phosphate rock annually. The relatively small islands forming the Japanese empire proper have an area only a little larger than that of the British Islands, but a population over one and a half times greater. Intensive agriculture is necessary therefore to produce the crops needed to feed the people and the bulk of the phosphate rock was consumed in the manufacture of fertilizer.

Ocean and Nauru Islands[2, 11]

In the Gilbert group are the British Islands of Nauru and Ocean just south of the equator near Longitude 167° East. On these two islands are sizeable deposits of phosphate. They are operated by the British Phosphate Commission for the joint account of Great Britian, Australia, and New Zealand.

Nauru Island is 16 miles south of the equator and about 2,200 miles from Sidney, Australia. It has a total area of less than 12 square miles, most of which is phosphate bearing. A strip of land along the coast from 100 yards to a quarter of a mile in width is relatively level, but beyond this belt the land rises to a height of over 200 feet. The elevated portion of the island consists almost entirely of phosphate rock and coral pinnacles.

The phosphate was recognized as such about the year 1900 and exploitation began in 1906. The phosphate beds are surface deposits with little or no overburden, but the rock must often be dug from around the coral pinnacles, thus involving considerable hand labor. Nauru Island rock ranges in grade from 83 to 87 per cent in calcium phosphate (BPL).

Ocean Island is only about one-third the size of Nauru, but the phosphate occurs under the same conditions, is of similar origin, and of an equal grade. The rock on this island was discovered somewhat earlier than that on Nauru and exploitation started in 1900. The best deposits are found on the central table land where the phosphate beds extend to a depth of 30 feet or more.

The phosphate is mined by first removing the light overburden and then breaking out the rock with mechanical shovels as well by hand labor. The excavated phosphate is then loaded into skips which are elevated by a cable way carried to a head tower and dumped into a hopper. From here the rock is loaded into side dumping trucks and carried to wet storage bins. The rock is then crushed, screened and dried for shipment.

The mines on these islands were well managed and equipped with modern machinery, but when they fell into the hands of the Japanese in 1942 the mining and loading facilities were badly damaged.

The equipment, however, is now being rehabilitated and production has

risen markedly. The output from these islands in 1940 was 1,263,000 metric tons, of which the bulk was mined on Nauru. In 1949 the combined production of these islands (based on exports) was 1,067,000 tons.
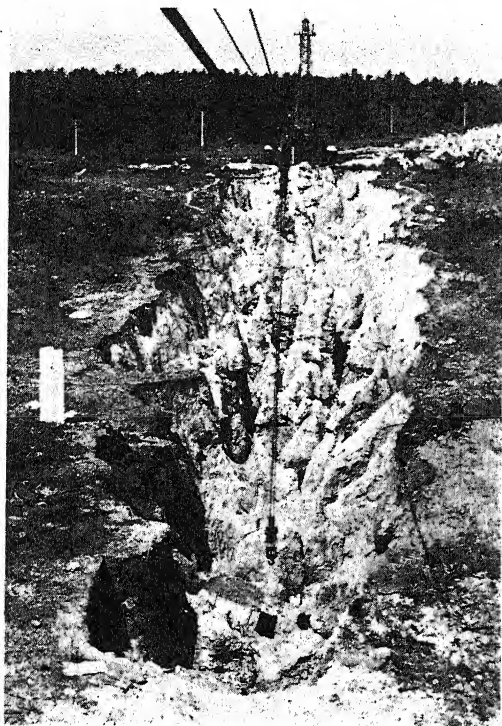
(Courtesy of International Minerals and Chemical Corporation, Ltd.)

FIGURE 7. Mining high-grade phosphate rock on the island of Nauru.
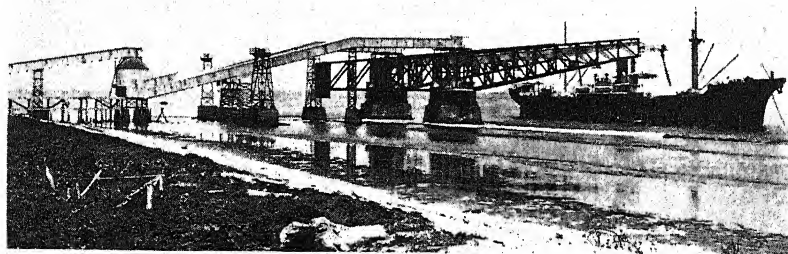
(Courtesy of International Minerals and Chemical Corporation, Ltd.)

FIGURE 8. Loading facilities for phosphate rock on the islands of Nauru. Since there are no harbors, vessels must anchor and in rough weather must put out to sea.

One of the greatest problems in the development of the Nauru and Ocean Island deposits was the lack of harbors for deep draft vessels, necessitating loading in the open sea. This difficulty was partly overcome by the construction at Nauru of a cantilever loading pier reaching beyond the outer edge of the coral reef surrounding the island. This arrangement permitted the rock to be loaded rapidly and cheaply.

Makatea Island[8, 11]

The small island of Makatea is one of the Society group about 120 miles north of Tahiti. It has an area of only 1,200 acres, but much of it contains

(Courtesy of International Minerals and Chemical Corporation, Ltd.)

FIGURE 9. Phosphate mine on Makatea Island. Much of the phosphate rock is mined by hand labor.

phosphate rock similar in character and grade to that on Nauru and Ocean Islands. The deposits are owned or controlled by the Anglo-French Phosphate Company. The island is rather heavily wooded, but the phosphate occurs near the surface and after the land is cleared, it is rather cheaply mined. The grade of phosphate ranges from 80 to 82 per cent tricalcium phosphate with a low content of iron and aluminum oxides. The rock is then hauled by train to a crushing and drying plant where it is stored for shipment.

Prior to World War II (1939) the output of Makatea phosphate amounted to 161,000 tons, but after the capture of Ocean and Nauru Islands by the Japanese, the production of Makatea phosphate was stepped up to help meet the shortage of fertilizers in Australia and New Zealand. The shipments of phosphate from this island in 1948 are estimated at 185,000 tons.

Christmas Island[11]

This island, which is under British control, is situated in the Indian Ocean about 190 miles southwest of Java. It has an area of less than 60 square miles. Like Makatea, this island is rather densely wooded.

The phosphate deposits of Christmas Island are similar in many respects to those of the Pacific Islands and the grade of the rock is fully as high (averaging well over 80 per cent tricalcium phosphate). Limestone pinnacles that occur in the phosphate beds render it necessary to employ much hand labor.

The phosphate is carried by tram cars drawn by small diesel locomotives, dumped over $2\frac{1}{2}$-mesh screens into hopper cars. The coarser materials are fed to jaw crushers, screened, and loaded into separate hopper cars. The crushed rock containing from 8 to 25 per cent moisture is then sent to the port about 12 miles from the mines where it is passed through rotary oil-fired driers and the moisture reduced to 2 to 3 per cent. The dried product is then loaded into storage bins, from which it feeds onto fast moving belts that run to the loading piers and discharge the rock direct into vessels moored alongside.

As is the case with most of the phosphate-bearing islands, shipment of the rock is handicapped by lack of harbors and the great depths of water. Ships are held away from the piers by costly mooring buoys, and in rough weather it is often necessary for them to put to sea to avoid being wrecked.

Just before Christmas Island was taken over by the Japanese, the British demolished the mining and loading facilities, but these have been largely restored and production of phosphate rock resumed. Shipments in 1949 were close to 239,000 tons.

According to a recent report[1], an agreement between the Australian and New Zealand governments is being considered for the purchase of the phosphate leases on this island.

Curacao[11]

Although phosphates are found in many islands in the Caribbean Sea, only the Dutch Island of Curacao, off the cost of Venzuela, contains known deposits of present commercial importance. The phosphate occurs on a hill near the seacoast at Fuick Bay, and is said to cover an area of about 60 acres at a depth of 60 to 70 feet. Prior to 1932 the grade of rock mined on Curacao ranged from 85 to 87 per cent BPL, but at that time rock containing 77 to 79 per cent BPL began to be developed and now most of that shipped is of this latter grade. Curacao phosphate contains less than 1 per cent of iron and aluminum oxides and is much lower in fluorine than that from Florida, Tennessee and the western states. Small tonnages are imported into the United States for use in stock feeds.

After World War II the annual output of Curacao phosphate averaged 100,000 tons over quite a period, but as the highest grade rock neared exhaustion, production fell off somewhat. In 1939 exported totaled 64,000 tons but dropped to 9,000 tons in 1945. The production in 1949 was estimated at 65,000 tons.

Other small West Indian islands that have produced phosphate in the past are Aruba, Redonda, Navassa and Sombrero. Their present output is small and in the case of Redonda and Navassa the phosphate is so high in iron and alumina that it is considered unsuitable for the manufacture of superphosphate.

Canada, Mexico and South America

Canada

While the bulk of the phosphate rock consumed in Canada is imported from the United States, deposits of Pre-Cambrian apatite occur in the Ottawa-Kingston region of Ontario and Quebec. These deposits were of considerable importance before the development of the Florida phosphate fields, but production now amounts to only a few thousand tons. Most of the rock is used locally by the Electric Reduction Co., Buckingham, Quebec, for the manufacture of elemental phosphorus by the electric furnace process. The only other known phosphate in Canada is a low-grade sedimentary deposit of phosphorite just west of the boundary between southern Alberta and British Columbia. This deposit was worked during World War II.

Mexico[11]

Low-grade phosphate deposits of Jurassic or Cretaceous age occur in various parts of Mexico, but few have proved of commercial importance. The only one which has been exploited to any extent is near Monterrey in Zacatecas. This rock is used in the manufacturer of low-grade superphosphate at El Vergel, Durango.

Brazil

Although the reserves of phosphate rock in Brazil are reported to be large the deposits have been exploited to a very limited extent. According to Noyes[11], several thousand tons of apatite a year are being produced from deposits at Ipanenia, San Paulo, where apatite is recovered in the form of a high-grade concentrate by removing the iron present with magnetic separators, but as far as known, little if any of the phosphate rock is exported. Leonardos[10] lists eighteen localities having commercial or near commercial deposits of apatite, phosphorite, aluminum phosphate and guano.

Chile[11]

Apatite deposits also occur on both slopes of the Coast Range between Copiapo on the north and Coquimbo on the south. The rock is calcined with sodium nitrate or sodium sulfate yielding a product similar to Rhenania phosphate containing 24 to 25 per cent of citric soluble P_2O_5.

ASIA

Although phosphate deposits have been reported in various parts of Asia, many are merely of local importance and few have been extensively developed.

China[11]

In 1924 some high-grade apatite deposits were discovered in the province of Kiangsu, eastern China, but mining operations were on a limited scale until the Japanese took over this area and stepped up mining operations to about 50,000 tons per year. The rock is said to average 75 per cent BPL. A deposit containing 2,000,000 tons of apatite was reported discovered during World War II in Yunnan Province near the south end of Kungan Lake. The confused situation in China makes the systematic development of its phosphate resources rather unlikely.

Indochina[11]

Small deposits of phosphate rock are found in several places in Indochina, and French interests worked them to a limited extent for a number of years prior to World War II. The rock varies greatly in composition (37 to 74 per cent BPL), and hence the average grade is too low for the manufacture of superphosphate. According to Noyes[11] the production in 1939 amounted to 35,694 metric tons which was finely ground and applied directly to the soil.

An apatite deposit in the Lao Kay region, northwestern Tonkin, approximately 250 miles by rail from the port of Haiphong was exploited by the Japanese during the War and in 1942 it was reported that 100,000 tons were produced. The installations, however, were subsequently heavily bombed and partially destroyed. It is doubtful therefore, if such a tonnage can be mined again for some years.

India[9]

A number of small apatite deposits occur in various parts of India. The better known ones are located in the copper belt of Dhalbrum (eastern Singhbhum) where the apatite is associated with magnetite. In addition, spotty occurrences of phosphate nodules are found in an area of 11 to 12 square miles to the southeast and northeast of Uttatur, 20 miles from

Trichinopoly. The known deposits of India apparently are insufficient to supply the fertilizer needs of that vast country, but the government is stressing the importance of establishing a phosphate industry and is weighing the relative merits of the several processes for treating bones and phosphate rock to render phosphoric acid available to crops.

Asiatic Russia[3]

The largest deposits of phosphate rock in Asia are said to be in the Kazak Republic of Soviet Russia. In 1931 the reserves of rock in this area containing from 20 to 42 per cent BPL were estimated at 1,321,568,000 metric tons distributed as follows: Aktyubinsk district, 706,000,000 tons; the West Kazak district, 460,236,000 tons; and the South Kazak district, 155,000,000 tons. No actual production figures are available.

Other deposits have been reported in the Kara-Kalpak and Tadzhik Republics of Asiatic Russia with reserves amounting to nearly 20,000,000 metric tons of phosphate rock containing from 26 to 55 per cent BPL. It is not known to what extent these phosphates are being exploited but if the rock can be economically beneficiated, processed and distributed, the deposits should be of great importance in the development of a vast agricultural area.

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10. Elemental Phosphorus and Its Manufacture

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INTRODUCTION

Thirty years ago the bulk of phosphoric acid and its compounds were produced by the action of sulfuric acid on phosphate rock. Only a relatively small tonnage of pure acid and high-grade chemicals were derived directly from elemental phosphorus.

This was caused by the incomplete development of thermal methods for the reduction of phosphate rock and to the apparent economic superiority of sulfuric acid as a reagent in producing phosphoric acid and phosphates for fertilizer purposes.

In recent years more favorable electric power rates, improvements in furnace design, and the general adoption of the Cottrell electrical precipitator[23] as a means for collecting the P_2O_5 evolved in the combustion of phosphorus, have contributed to the successful development of thermal reduction methods, and now the bulk of the phosphoric acid employed for food and chemical purposes is derived from elemental phosphorus.

As the medium through which pure concentrated phosphoric acid may be produced, phosphorus is of interest to all potential consumers of high-grade phosphate products, and descriptions of the methods employed in manufacturing this element are an essential part of any treatise on phosphoric acid.

A REVIEW OF METHODS FOR PRODUCING PHOSPHORUS

While the production of phosphorus has always depended on the volatilization of this element from its compounds under reducing conditions, in the early days of its manufacture the system employed was elaborate, cumbersome, and costly[22]. It involved: (1) the treatment of phosphate of lime with sulfuric acid; (2) the separation by filtration of the phosphoric acid thus obtained; (3) the concentration of this acid by evaporation; and (4) the mixing of this acid with charcoal or coke and heating the mixture to high temperatures in clay retorts. Practically every step entailed some

loss of the material sought, so the recovery of the phosphorus was very incomplete.

According to Readman[22], the substitution of silica for sulfuric acid to obtain phosphorus directly from phosphates of lime was first proposed by Auberton and Boblique in 1867, when these investigators took out a patent covering the volatilization and collection of elemental phosphorus from pulverized mixtures of phosphate rock, sand and coke heated to a high temperature in closed containers. One year later (1868) Brison[1] advocated the use of a blast furnace for smelting natural phosphates and producing elemental phosphorus; in 1879 Serve took out a patent in which he proposed the use of blocks or bricks of an intimate mixture of phosphates and silica bound together by pitch, tar, or coal and smelted in a blast furnace. In 1889 Readman[21] proposed to produce elementary phosphorus by heating in an electric furnace (from which air was excluded) a misture of phosphorus-yielding material (in solution), sand and coke. Two years later (1891) in an address before the Society of Chemical Industry[22], this inventor stated that he had found it was unnecessary to dissolve the phosphate mineral with sulfuric acid before furnacing, since a mixture of sand and coke decomposed it completely at the temperatures attained in the electric furnace. This general scheme is almost universally employed today in the manufacture of phosphorus. The processes of Wing[38], G. C. Landis[15], and Haff (12) are similar to that proposed by Readman, since (with the exception of that of Wing) they all deal with the production of phosphorus by smelting mixtures of phosphate rock, sand, and coke in an electric furnace. Wing and Landis, however, claimed advantages for briquetted or molded charges on the basis that the temperature was more easily controlled, dust avoided, and a purer product recovered. Van Ruymbeke[30], appears to have been the first in this country to patent a furnace process for the recovery of phosphoric acid rather than phosphorus. He advocated the use of a blast furnace for treating mixtures of phosphate rock, a reducing agent, and an acid flux, introducing into the upper part of the furnace sufficient air to oxidize the elemental phosphorus evolved.

Hechenbleikner[13] proposed making up an electric furnace charge of phosphate rock, coke and a potash-bearing feldspar (in lieu of silica or sand) in order to produce both potash and phosphorus. The economic possibilities of employing silica in the form of green-sand, potash shales, orthoclase and other potash-bearing silicates in the furnace process have also been investigated by Ross, Mehring and Jones[24]. These investigators showed that both potash and phosphorus can be driven off even at relatively low temperatures provided strict reducing conditions are maintained in the reacting mass. Peacock[19] heated mixtures of phosphate rock and carbon in an atmosphere of nitrogen, claiming that phosphorus and carbonitrides

are produced which can be converted into ammonia and ammonium phosphate by treatment with steam. No particular type of furnace is specified by this inventor. As far as known, however, there has been no commerical application of this process.

With a view to the simultaneous production of ferrophosphorus and phosphoric acid or other phosphorus compounds, J. J. Gray[11] proposed to smelt a mixture of phosphate rock, silica, coke, and iron ore in an ordinary blast furnace. The ingredients in the charge are so proportioned that while the maximum displacement of phosphorus from the phosphate rock is sought, the amount of iron added in the form of ore is insufficient to take up all of the phosphorus thus evolved. For a number of years, two blast furnaces for the production of ferrophosphorus were operated in Tennessee, but they are now closed down.

Washburn and Heckenbleikner each took out a great number of patents dealing with processes for the volatilization of phosphorus and with types of furnaces in which the reactions may be brought about. Space forbids detailed discussions of all these methods and apparatus, but they are listed in Table 13 of the Appendix.

Washburn[35] proposed to charge a mixture of phosphate rock, silica, and carbonaceous material into the shaft of a blast furnace, where the combustion of the fuel is effected and the mass brought to a state of fusion. The molten material is then run into the crucible of an electric furnace, where the final smelting of the charge and complete volatilization of the phosphorus is effected.

Several years later Washburn[36] described an apparatus in which certain features of both the blast and electric furnace are combined, and suggested a briquetted mixture of phosphate rock and silica in order to insure free passage of the gaseous products through the charge in the shaft. Air is introduced into the shaft to burn the combustible gases and evolved phosphorus and thus preheat the green charge.

Both Hechenbleikner[14] and Washburn[37] described furnaces in which the charge is fed through a rotary kiln and the preheated or partially smelted mass then run into the crucible of an electric furnace, where coke or some other carbonaceous material is added and the phosphorus driven off. By leading the hot and burning gases through the kiln countercurrent to the phosphate charge, heat economies are effected which cut down the energy required in smelting the material in the electric furnace.

Southgate[29] described a combined fuel and electric blast furnace in which the tuyeres are filled with granular coke and supplied with a suitable electric current. A mixture of air and combustible gas or oil is ignited and serves to carry the current into the furnace. Thus he claimed the advantage of the combined effects of fuel and electric energy.

Principles Involved in Present Processes for Producing Phosphorus

In the manufacture of phosphorus from mixtures of phosphate rock, silica and carbon according to the present commercial processes two fundamental principles are involved:

(1) At high temperatures (1500 to 1800°C) silica assumes the properties of a relatively strong acid in so far as its ability to combine with bases is concerned, and therefore it can displace the phosphoric acid of phosphate rock forming silicates of lime and free phosphoric anhydride (P_2O_5).

(2) When carbon or coke is added to the mixture to be smelted, elemental phosphorus and a molten calcium silicate slag are produced and if reducing conditions are maintained throughout the operation the decomposition of the rock and expulsion of its phosphorus content may be brought about at temperatures ranging from 1,300 to 1,500°C.

According to Nielsen[18] tricalcium phosphate and silica begin to react at a temperature of 1,150°C and continue to form various compounds up to 1,650°C. Unless a reducing agent is present, however, these chemical changes merely consist in certain combinations of the two substances and no phosphoric acid is evolved. This same author states that while CO will not reduce tricalcium phosphate this latter compound is completely reducible by carbon, the reduction beginning at 1400°C. He claimed, however, that some phosphorus always remains in the residue because the CaO formed unites with the undecomposed calcium phosphate to form more basic compounds of phosphoric acid which are not reduced by carbon. Peacock took issue with Nielsen on this point, stating that if the evolved gases are removed as fast as they are formed, complete dispersion of phosphorus is obtained by heating mixtures of phosphate rock and carbon, and Ross, Mehring and Jones[24] state that if pure tricalcium phosphate mixed with one-fifth of its weight of carbon is heated to 1400°C in a reducing atmosphere, 96 per cent of the phosphorus contained therein is volatilized, and if the temperature is carried to 1550°C, the evolution of phosphorus is complete.

The presence of a reducing agent is essential, however, in order to bring about the volatilization of phosphorus at the lower temperatures. Some early investigators as well as the writer observed that by heating finely ground mixtures of phosphate rock, silica, and coke under reducing conditions the volatilization of phosphorus begins considerably below 1,300°C, and by prolonged heating at this temperature the bulk of this element may be driven off.

Ross, Mehring and Jones[24] calculated the decomposition temperatures of calcium phosphate and carbon with and without the addition of various

proportions of silica and found that these calculated temperatures checked fairly closely with those observed in actual experiments.

Table 1 is part of one taken from the article just cited. A study of Table 1 shows that fewer calories and lower temperatures are required where calcium phosphate is mixed with silica and carbon in the proportions given in equations (4) and (5) and as the ratio of silica to lime drops below these levels the temperature required increases.

Whereas, various silicates of lime are no doubt formed in smelting mixtures of calcium phosphate, silica and carbon, depending on the silica-lime ratio in the charge, the general course of the reaction is usually rep-

TABLE 1. DECOMPOSITION TEMPERATURE OF CALCIUM PHOSPHATE IN REACTION WITH SILICA AND CARBON, UNDER A PRESSURE OF ONE ATMOSPHERE

Reaction	Calories	Temp.	Silica–Lime Ratio (SiO/CaO	Phos.–Carbon Ratio P/C
(1) $Ca_3(PO_4)_2 + 5C \rightarrow 3CaO + P_2 + 5CO$	418,900	1,385		2.37
(2) $Ca_3(PO_4)_2 + 8C \rightarrow Ca_3P_2 + 8CO$	*664,920	1,690		1.48
(3) $Ca_3(PO_4)_2 + 8C \rightarrow 3Ca + P_2 + 8CO$	749,920	1,680		1.48
(4) $Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow CaO \cdot SiO_2 + P_2 + 5CO$	365,350	1,190	1.07	2.37
(5) $Ca_3(PO_4)_2 + 2SiO_2 + 5C \rightarrow (CaO)_3(SiO_2)_2 + P_2 + 5CO$	*368,900	1,200	0.72	2.37
(6) $2Ca_3(PO_4)_2 + 3SiO_2 + 10C \rightarrow 3(CaO)_2 \cdot SiO_2 + 2P_2 + 10CO$	752,900	1,260	0.54	2.37
(7) $Ca_3(PO_4)_2 + SiO_2 + 5C \rightarrow (CaO)_3 \cdot SiO_2 + P_2 + 5CO$	390,350	1,280	0.36	2.37

* Estimated.

resented by the following simple equation:

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + P_2 + 5CO.$$
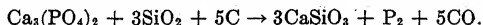
The presence of various impurities in phosphate rock change the heat requirements and the character of the slag produced, but in general the reactions are assumed to take the above course and the furnace charge is proportioned accordingly.

THE ELECTRIC FURNACE PROCESS FOR ELEMENTAL PHOSPHORUS

Since the consumption of phosphorus as such in time of peace is relatively small, the production of this element was rather limited until its value as a source of pure phosphoric acid was fully appreciated. Impetus was given to the manufacture of phosphorus over thirty years ago (1917 and 1918) when Ross et al.[23] and Carothers[2] of the Bureau of Soils, U. S. Department of Agriculture, published the results of certain pilot plant experiments

conducted in electric furnaces using mixtures of Florida phosphate rock, silica sand and coke. The phosphorus evolved was oxidized directly and converted into phosphoric acid, which was collected in a Cottrell precipitator. This work encouraged commercial developments along the same lines, but it was not until the Tennessee Valley Authority[3, 4, 5, 6, 7, 17, 34], the Monsanto Chemical Co. and the Victor Chemical Works undertook the systematic investigation of various types of electric furnaces and auxiliary equipment that the manufacture of elemental phosphorus as an intermediate in the production of phosphoric acid was developed on a large commercial scale.

TABLE 2. PRODUCERS OF ELEMENTAL PHOSPHORUS IN THE UNITED STATES AND THEIR ESTIMATED ANNUAL CAPACITIES*

Producer	Location	Estimated Annual Capacity (Short Tons)	Per cent of Total
Monsanto Chemical Co.	Columbia, Tenn.; Monsanto, Tenn.	60,000	31.2
Victor Chemical Works	Mt. Pleasant, Tenn.; Tarpon Springs, Fla. Silver Bow, Mont.	57,000	29.6
Tennessee Valley Authority	Wilson Dam, Ala.	20,000	10.4
Westvaco Chemical Division	Pocatello, Idaho	30,000	15.6
Oldbury Electro-Chemical Co.	Niagara Falls, N. Y.	8,000	4.1
Virginia-Carolina Chemical Co.	Nichols, Fla.; Charleston, S. C.	14,000	7.3
American Agricultural Chemical Co.	South Amboy, N. J.	3,500	1.8
Total		192,500	100.0

* Several additional phosphorus furnaces have either been projected or are now in the course of construction.

Today, in addition to the TVA, six fertilizer and chemical companies in the United States are producing elemental phosphorus in electric furnaces. However, most of the product is being converted into phosphoric acid and pure phosphate compounds. As shown in Table 2, the estimated capacity of these plants in 1951 was 192,500 short tons, requiring the equivalent of about 1,380,000 tons of medium-grade phosphate rock (32 per cent P_2O_5). The growth of the phosphorus industry from 1930 to 1951, as well as the estimated capacity up to and including 1953 is shown in Figure 1.

Composition of Furnace Charge

The charge for an electric furnace producing elemental phosphorus varies somewhat, depending upon the type and composition of the phosphate

rock employed, but the siliceous flux added is adjusted so that the SiO_2 and CaO bear a definite relation to one another. The amount of carbon added (as coke) is sufficient to reduce the P_2O_5 and Fe_2O_3 present to phosphorus and metallic iron respectively. These ratios range approximately between the following limits:

$$SiO_2/CaO \rightarrow 0.8 \text{ to } 1.2$$

$$P_2O_5/C \rightarrow 2.3 \text{ to } 2.6$$

A typical furnace burden for the production of elemental phosphorus
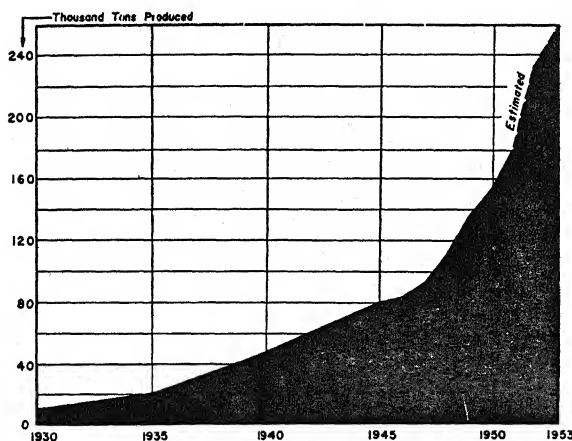
FIGURE 1. Chart showing the phenomenal growth of the phosphorus industry (1930–1951).

comprising high-grade phosphate rock and silica pebbles has the following approximate composition (Table 3).

Since high-grade phosphate rock contains from 32 to 37 per cent P_2O_5, 40 to 48 per cent CaO and only from 5 to 10 per cent SiO_2, it is obvious that it must be diluted with substantial quantities of sand or gravel in order to obtain a furnace charge having the proper silica-lime ratio for smelting purposes. Waggaman and Wagner[32] were the first to suggest the use of lower grade siliceous phosphates in making up an electric furnace charge, pointing out that it is often more economical to employ run-of-mine phosphates direct, rather than to selectively mine high-grade rock or incur the expense of beneficiation, only to add or return the main impurity (SiO_2) for fluxing purposes. The use of lower grade phosphates in making up an electric furnace charge is rather general practice except where long hauls are involved in bringing the rock to the reduction plant.

Preparation of Furnace Charge

Both the electric and blast furnace processes for the manufacture of phosphorus or phosphoric acid require a phosphate charge in lump form. The reasons for this are that fine material tends to block the passage of the phosphorus and gases evolved and cause bridging and uneven descent of the furnace stock, resulting in puffs and the carrying over of excessive quantities of dust.

Whereas, some phosphate deposits yield a fairly high percentage of lump rock, the crushing of this material to the proper size for furnace treatment always involves the production of a considerable proportion of fines.

TABLE 3. TYPICAL BURDEN FOR AN ELECTRIC FURNACE PRODUCING ELEMENTAL PHOSPHORUS

Proportions of raw materials	High grade phosphate rock	2,000 lbs
	Silica pebbles	718 lbs
	Coke (85% carbon)	324 lbs
		3,042 lbs

| Ingredients | Analysis (%) | | | Final Composition of Charge |
	Phosphate Rock	Silica Pebbles	Coke	
P_2O_5	34.0			22.7
CaO	45.0			29.6
SiO_2	5.0	98.0	6.0	27.0
Fe_2O_3	3.5			2.3
Al_2O_3	4.0	1.0	7.0	3.8
CO_2	2.0			1.3
F	3.0			2.0
H_2O	1.5	1.0	1.0	1.3
Carbon			85.0	9.1

Again, modern methods of beneficiation (particularly flotation) now recover very finely divided phosphate rock (1 mm and finer), which is unsuitable for direct use in the furnace processes; finally, much of the run-of-mine phosphate (matrix or muck) and lower grade phosphatic shales, though having a chemical composition approximating that required for furnace treatment, also contain high proportions of fine material.

It is obvious therefore, that for the full and economic operation of a phosphorus plant at least part of the phosphate rock must be treated before it is charged to the furnace.

Four general methods of preparing lump material from phosphate fines have been proposed and practiced on a commercial scale:

(1) Pelletizing by tumbling or extrusion.
(2) Agglomeration by nodulizing at high temperatures.

(3) Sintering a mixture of phosphate fines and coke.

(4) Briquetting with the addition of a suitable binder.

Detailed descriptions of these various methods, based on both pilot plant experiments and operations on a commercial scale, have been published in a comprehensive report by the staff of the TVA[23a], but a brief discussion of their relative merits and applicability follows:

Pelletizing. Pelletizing may be brought about by pugging the finely divided phosphate rock with water followed by either extrusion (under pressure) through small openings or tumbling the dampened material in a rotary cylinder to form rounded pellets. In either case the pellets are dried and preferably calcined to harden them so they will withstand the severe conditions imposed upon them in the furnace with a minimum amount of disintergration. Successful pelletizing of finely divided phosphate can only be efficiently accomplished in the presence of a binder and hence this method is particularly applicable to phosphate muck or matrix containing clay-like or plastic material. Baking or calcining the pellets is effected either in a shaft or rotary kiln at a temperature of approximately 1100°C.

The advantage of a pelletized charge is its uniform size which makes for smooth furnace operation; the main disadvantage is the extra step or preliminary pugging of the material which is neccessary to yield a product of uniform strength.

Nodulizing. Nodulizing consists in feeding finely divided phosphate directly to brick-lined rotary kilns and heating the material to incipient fusion (1250 to 1400°C) by the combustion of oil, gas or powdered coal introduced countercurrent to the phosphate rock. This results in the formation of nodules of various sizes which are subsequently discharged into an unlined rotary cooler, crushed and screened. The screenings or undersize ($-\frac{1}{4}$ inch) are returned to the kilns for retreatment.

One advantage of the nodulizing process is that no clay or other binder need be added to the phosphate fines and hence no preliminary pugging is necessary. This process therefore is applicable to a wider variety of raw materials than the pelletizing method. The disadvantage of nodulizing lies in the high temperatures required and the mechanical difficulties involved due to ringing in the kilns and the formation of oversize nodules that must be crushed and the fines returned for reprocessing.

A water-cooled boring bar is periodically inserted into the kiln to dislodge the partially fused material which builds up on the walls.

Sintering. As its names implies the sintering process consists in the incipient fusion of a porous bed of damp finely divided phosphate mixed with 10 to 12 per cent of coal or coke spread uniformly on an endless belt made up of cast iron herring-bone grate bars. The coal or coke in the mixture is ignited by an oil flame and continues to burn as the laden cast iron pallets pass over a series of wind boxes which draw the air down through the bed

of phosphate by means of an exhaust fan. Combustion of the coal or coke in the mass is effected in 10 to 20 minutes, depending upon the amount of fuel mixed with the phosphate and the rate at which the air is drawn through the material, but is completed before the sinter is discharged. As the pallets round the discharge end of the machine the sinter falls into a crusher where it is reduced in size to at least $1\frac{1}{4}$ inch. The crushed sinter is then fed upon a $\frac{1}{4}$-inch vibrating screen, the coarse material being conveyed to storage as furnace feed, while the $-\frac{1}{4}$-inch material is recycled to the sintering operation.

Sintering has the advantage of being applicable to a wider variety of natural phosphates than pelletizing, but in contrast to the nodulizing process, requires some mixing and preliminary treatment before it is spread upon the pallets. When relatively clean granular phosphate sand is used the material should be dampened and preferably pelletized after mixing it with a little clay-like binder to prevent it from running through the grate bars. If phosphate matrix or muck, containing a considerable proportion of plastic material is used, precautions must be taken that the material is not packed on the pallets and its porosity so reduced that insufficient air is drawn through the bed to burn the coke or coal. Properly prepared and sized sinter makes an excellent charge for either the electric or blast furnace.

Briquetting. The briquetting of the phosphate charge was first suggested as a means of utilizing run-of-mine phosphates containing appreciable quantities of a natural clay-like binder[31b]. Later, various types of added binders were employed to make the process applicable to high-grade phosphate sands containing no natural cementing material. A briquetted charge has been successfully employed in the phosphorus blast furnace[10a].

Briquetting entails a thorough mixing of the phosphate fines and the addition of sufficient water to form a damp mass. The optimum water content varies somewhat according to the nature of the raw materials but averages about 14 per cent. Coal or coke may be added to the mixture for reducing purposes but is not necessary, and in the case of coke is probably not desirable because of its abrasive nature. Briquettes for the electric furnace process should be dried or calcined, otherwise, the moisture in the charge increases the velocity of the evolved gases, lowers furnace efficiency and increases electric power consumption.

The briquetting process as conducted in the pilot plant of the TVA[29a] may be briefly described as follows:

The finely divided phosphate material is fed into a pug mill consisting of a trough 10 feet long, 32 inches wide and 23 inches deep. Two heavy revolving shafts fitted with mixing blades serve to knead the material to which approximately 14 per cent of water is added as the mass is advanced

toward the far end of the mixer where it is discharged upon a belt and conveyed to the hopper surmounting the briquetting rolls. This machine consists of two hardened steel rolls, $12\frac{1}{2}$ inches outside diameter, each fitted with 4 rows of matching pockets or molds. The rolls are driven at a speed of 4 to 5 rpm by a 5-h-p motor and the clearance between the rolls is $\frac{1}{16}$ inch or less. The pressure on the material as it is fed into the pockets of the revolving rolls ranges from 1,000 to 4,000 psi depending on the clearance between the rolls and the rate at which the material is drawn into the pockets. The briquettes are discharged from the lower part of the machine into a pan conveyor and pass to a kiln to be dried or calcined.

Briquetting has the following advantages: (1) A furnace charge of uniform size is thus obtained. (2) No subsequent crushing is required and no substantial percentage of fines are produced requiring to be recycled. (3) Excessive temperatures with their attendent disadvantages are avoided.

The disadvantages of briquetting are: (1) Necessity of pugging or preliminary preparation of charge. (2) Necessity of adding a binding material if none is present in the raw materials.

Choice of Agglomerating Process

In summing up the relative merits of the various methods of preparing a phosphate charge for furnace treatment the staff of the TVA[29a] concluded that "no agglomeration process can be recommended to the exclusion of the other processes since certain physical properties of the raw materials available may dictate a particular process."

It was concluded, however, that satisfactory agglomerates for use in the electric furnace can be produced cheaper either in the form of calcined pellets or as calcined briquettes than by either nodulizing or sintering. The experience of the writer however in the preparation of both briquetted and sintered phosphates leads him to believe that the latter process is as cheap as, or cheaper than any of the agglomeration processes described above.

Electric Furnace and Its Operation

A typical large commercial electric furnace (15,000 kw), having a daily (24 hour) output of 28 tons of phosphorus, consists of an oblong water-cooled steel shell 32 feet in length, 15 feet wide and 12 feet deep. The bottom of the furnace is composed of carbon blocks nearly 4 feet thick. The carbon lining extends up the walls to a point well above the slag pool. From this point a high-grade fire-brick lining (2'8" thick) is used. The furnace has a dome-like steel top with a cast refractory lining and is provided with suitable openings for the electrodes and for the introduction of the phosphate burden. This steel top is flanged and bolted to a similar

flange constituting the upper edge of the furnace crucible. Three 40-inch carbon electrodes, in line and equally spaced, are held in a vertical position by clamps and extend into the furnace through water-cooled glands. The narrow annular gap between these glands and the electrodes is packed with asbestos to minimize the escape of phosphorus or the entrance of air into the furnace. The copper electrode holders or clamps are cooled by circulating water and supplied with current from transformers located near the furnace.

As the electrodes are consumed, new lengths are added by means of short carbon male couplings which screw into the ends. These electrodes can be readily raised or lowered as furnace conditions require.

The phosphate rock, siliceous flux and coke breeze are fed from individual hoppers and properly proportioned on a conveyor belt which carries the mixture to several bins suspended above the furnace. From these bins it is fed through closed chutes or pipes and distributed uniformly over the full width and length of the furnace.

At one end of the furnace is an 18-inch opening connected with a steel unlined flue through which the gases and phosphorus vapor are led into two hot Cottrell precipitators. The precipitators remove the dust entrained in the furnace gases. Unless this dust is removed before condensing the phosphorus, impure sludges are obtained which are difficult to handle.

Hot Precipitators

These two precipitators which are connected in series have cast-iron shells lined with refractory brick. Electrical heating units are imbedded in the walls to keep the temperature well above the dew point of phosphorus (500 to 700°F). The upper and lower headers of these precipitators are connected by vertical steel pipes (collecting electrodes) 10 inches in diameter and 12 feet in length, with a single discharge electrodes of stainless steel wire down the center of each. Rapping devices are provided to dislodge the dust that accumulates on the collecting electrodes and this dust falls into a hopper which is periodically sealed off and its contents discharged. The precipitators operate at 35,000 to 40,000 volts and the power consumption averages only about one-third K.V.A. per 1000 cu ft of gas treated per minute.

The gases enter the lower header of the first of these precipitators and hence upward through the steel pipe at an average velocity of 5 linear feet per second. From the upper header of the first unit, they are led down to the lower header of the second unit, where the operation is repeated and practically all suspended particles are removed. The amount of dust collected varies with the nature of the phosphate charge, but averages about two tons per day. It contains approximately 22 per cent of available P_2O_5

and in some cases as high as 15 per cent of K_2O. When fully oxidized this dust is an excellent fertilizer material. The carbon monoxide gas and phosphorus vapor (substantially free from dust and solid impurities) then enter the top of a phosphorus condenser.

Phosphorus Condenser

The phosphorus condenser consists of an unlined steel tower 30 feet in heigth and 4 feet in diameter fitted with 3 banks of non-clog water sprays encircling the condenser and discharging water into the tower at the rate of 150 gallons per minute. The gases are thus cooled, scrubbed, and the phosphorus condensed to a heavy liquid which settles out and is discharged along with the condensing water into a sump. The condensing water which is recirculated maintains a fairly constant temperature (135 to 140°F), and as acidity develops it is neutralized by the addition of soda ash. The pH is maintained at 5.5 to 6.0.

The phosphorus is periodically removed from the sump by means of a Gould submerged pump and sent to storage tanks maintained at a temperature high enough to keep the element in liquid form. The phosphorus thus collected is sufficiently pure to be used in the manufacture of phosphoric acid but may be more highly purified by passing it through sand filters or by chemical treatment. It can be pumped through steam-jacketed pipelines and loaded directly into tank cars for shipment or can be converted into phosphoric acid by forcing it through orifices and burning it in a combustion chamber as described in a subsequent chapter.

The wet gases, after passing through the condenser still contain a small quantity of suspended phosphorus which is whipped out by passing them through Nash vacuum pumps. The water containing this residual phosphorus is also discharged into the phosphorus sump. From the Nash pump the gas consisting of fairly pure CO may be burned directly in a kiln to furnish part of the fuel required to nodulize the phosphate charge or its thermal value utilized for power production.

The phosphorus recovery amounts to approximately 92 per cent of that originally present in the phosphate charge and the power consumption averages 13,200 kw hours per ton of phosphorus collected.

Of the remaining 8 per cent of phosphorus, part is combined with iron in the form of ferrophosphorus and the balance is left in slag. Under favorable conditions both the slag and ferrophosphorus are marketed as byproducts.

Figure 2 is a view of the upper part of a modern electric furnace for the manufacture of elemental phosphorus showing the electrodes, charging devices and the off-gas main. Figure 3 shows the tapping of the slag from such a furnace and Figure 3a shows liquid phosphorus being loaded into a tank car for shipment.

The Blast Furnace Process

Whereas the production of elemental phosphorus by treating phosphate rock in a blast furnace was proposed by Brison[1] as far back as 1868, there there is no record that this proposal was put into practice for over 50 years. Van Ruymbeke[30] was issued a patent in 1895 covering the smelting of phosphate rock and an acid flux in a blast furnace, but the object of this invention was to produce phosphoric acid, since air was introduced into the upper part of the furnace shaft to oxidize the volatilized products.

The first recorded investigational work on the production of phosphorus

A	– Furnace Roof
B	– Feed Spouts
C	– Cooling Water
D	– Electrodes
E	– Electrode Clamp
F	– Electrode Hoist
G	– Electrode Guide
H	– Gas Offtake
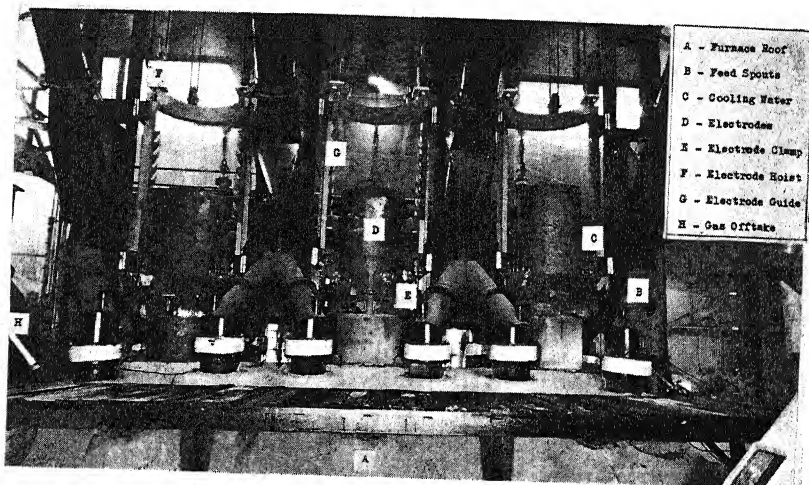
(Courtesy of TVA)

FIGURE 2. A modern phosphorus electric furnace, showing the electrodes and method of introducing the stock. The gas off-take is at the extreme left.

and phosphoric acid in a fuel-fired furnace was conducted by the writer and his co-workers[33] in 1920, and this process was later developed on a commercial scale by the Victor Chemical Works, Chicago, Ill., and by the Coronet Phosphate Company, New York, N. Y.

During the period 1927–1932 further experiments were conducted on a pilot-plant scale by Royster and his co-workers[25, 26] with a view to increasing the efficiency of the blast furnace process and the simultaneous volatilization of potash and phosphorus from mixtures of phosphate rock and potash-bearing silicates. These semi-commercial experiments were later continued by the TVA to compare the relative economies of the electric furnace and blast furnace processes. Pike[20] also reported investigation of a process for producing both phosphoric acid and potash in a blast furnace and con-

cluded that such a process would be economically attractive, particularly if an oxygen enriched blast was employed for burning the coke.

A – Feed Bin

B – Electrode

C – Gas Offtake

D – Slag Taphole

E – Ferrophosphorus Taphole
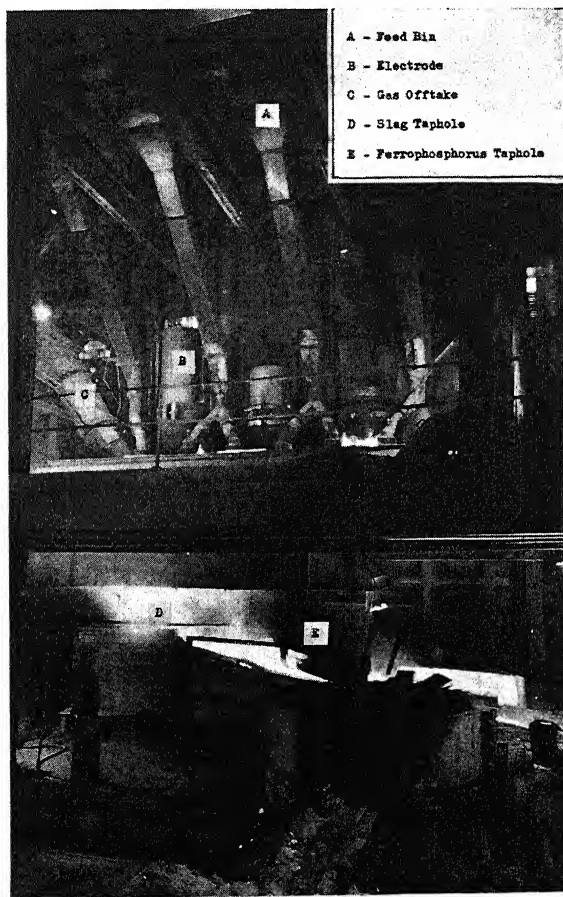
(Courtesy of TVA)

FIGURE 3. Tapping the slag from a modern phosphorus electric furnace.

Blast Furnace Plant and Its Operation

Much of the equipment employed for a phosphorus blast furnace is of the same general type as that required in the manufacture of pig iron, consisting of a boiler plant for generating steams from the surplus gas, a blowing engine for delivering air under pressure, a blast furnace of more

or less standard design and a series of stoves for heating the air delivered to the furnace for combustion of the coke fuel.

The main difference between a pig iron furnace plant and one employed for the manufacture of phosphorus lies in the elaborate dust collecting and condensing system required in the latter plant to insure the recovery of phosphorus before the gases pass to the boiler and heat regenerative equipment.

A phosphorus blast furnace should have a capacity of not less than 15
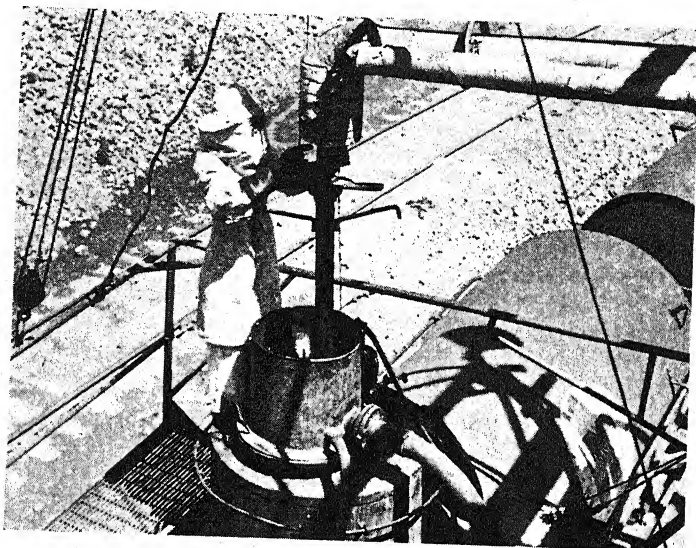
(Courtesy of Monsanto Chemical Co.)

FIGURE 3-a. Loading liquid phosphorus into a tank car for shipment. The liquid phosphorus is pumped into the car through a steam-jacketed pipeline, a layer of water being maintained over the phosphorus at all times. Elaborate precautions are taken to prevent fire and protect the workmen.

tons of elemental phosphorus per day (24 hours) and a larger plant is desirable to cut down heat radiation losses and obtain maximum fuel efficiency. A furnace of the above capacity has the following approximate dimensions: Hearth diameter (lined), 8'0"; bosh diameter (lined), 13'0", and stock line diameter 9'0". The over-all height of such a furnace is about 75' and its working volume is rated at 6,400 cubic feet. The hearth is lined with 36" of high-grade fire brick; the brick lining of the crucible walls is 18" thick, the bosh $13\frac{1}{2}$" and the inwalls $22\frac{1}{2}$" thick.

The furnace is equipped with a skip hoist, a double bell charging device and a lined down-comer for leading the volatilized products into the dust collecting system. To remove the dust a large refractory lined dust catcher is employed followed by several vortex or centrifugal cleaners. To insure

complete elimination of dust, however, it is desirable to have two or more Cottrell precipitators in parallel operated at a temperature well above the dew point of phosphorus.

Since the heat required for the phosphorus blast furnace is derived from the combustion of fuel, the volume of gas to be handled per unit of phosphorus volatilized is 7 to 8 times greater than that from an electric furnace, hence the dust collecting and phosphorus condensing systems must be proportionally increased in size. Moreover, the dew point of phosphorus is such that the temperature of the gases carrying such a small proportion of phosphorus must be reduced far below that of the gases from an electric
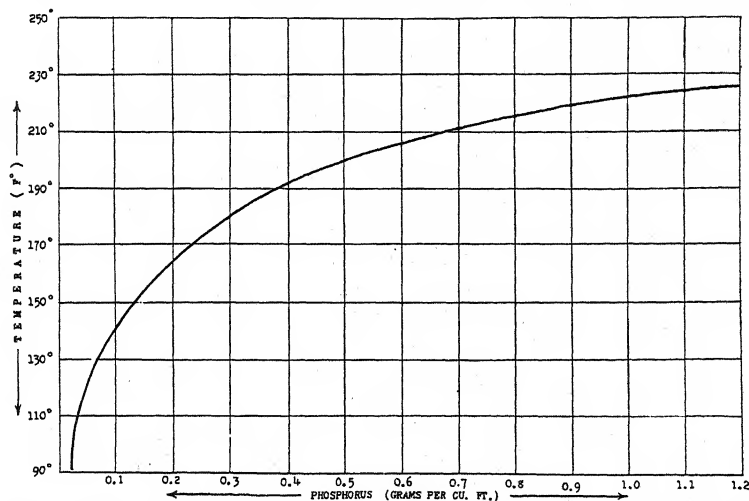
FIGURE 4. Saturation pressure of P_4 at various temperatures. (Quantity of phosphorus in gas in g cu ft.)

furnace to insure substantially complete recovery of this element. This means the use of cooler water in the final condensing unit.

Figure 4 shows the weight of elemental phosphorus (in grams) per cubic foot of gas saturated with phosphorus vapor at various temperatures. It is obvious that the blast furnace gas must be cooled below 100°F to insure condensation for the small proportion of this element contained therein.

In one of the phosphorus plants operated by the writer, the water from the final condenser was cooled by the Gensecke vacuum cooling system before being recirculated.

The condensed liquid phosphorus is pumped from a sump into storage tanks and either shipped in elemental form or oxidized to produce phosphoric acid.

After passing through the condensers a portion of the furnace gas (con-

taining 25 per cent CO) is burned under boilers for the generation of steam and a portion passes to the stoves, which serve the dual purpose of burning the gas and preheating the air for the blast furnace. This hot blast is delivered to the furnace at an average temperature of 1,480°F under a pressure of from 10 to 20 psi.

Royster and his co-workers[26] pointed out the economic advantage of using more highly heated air for the combustion of coke in a blast furnace, and designed a stove for this purpose partly filled with silica pebbles as a heat absorptive medium. The furnace gas along with the proper quota of air is introduced (under pressure) into the top of such a stove and burns downward. The hot products of combustion in passing through the pebble

TABLE 4. ESTIMATED MATERIAL REQUIREMENTS IN PHOSPHATE SMELTING PER TON OF P_2O_5 REDUCED (TWO TYPES OF FLORIDA ROCK)

Blast Temp.[1] (°F)	Washed Florida land-pebble phosphate (31.63% P_2O_5)			Florida hard-rock waste-pond phosphate (22.91% P_2O_5)	
	Coke[2]	Phosphate	Gravel[3]	Coke[2]	Phosphate
	Tons	*Tons*	*Tons*	*Tons*	*Tons*
500	11.45	3.68	0.36	11.70	4.85
1,000	4.91	3.68	.80	4.95	4.85
1,500	3.22	3.68	.91	3.24	4.85
2,000	2.45	3.68	.96	2.46	4.85
2,500	2.00	3.68	.99	2.02	4.85

[1] Blast humidity, 0.01 pound of water per pound of air.
[2] Fixed carbon, 87 per cent.
[3] SiO_2, 95 per cent.

bed heats it to a much higher temperature than that attained in the conventional two-pass checker brick stove.

Estimates of the coke requirements per ton of P_2O_5 reduced to elemental phosphorus at various blast temperatures are given in Table 4. The same data are shown diagramatically in Figure 5.

According to these estimates the quantity of coke required (per ton of P_2O_5 reduced) when employing an air blast at 2500°F, should be only 2 tons, as against more than 3 tons where the blast temperature is about 1500°F.

The pebble stove, however, can only be successfully used where the furnace gas is practically free from dust and phosphorus vapor. Such dust as well as P_2O_5 exert a fluxing action on the silica pebbles at high temperatures. So far this type of stove has not been widely employed in industry.

Normally the average recovery of phosphorus in the blast furnace process is approximately 88 per cent of that contained in the furnace charge, or about 4 per cent less than that recovered in the electric furnace process.

Part of the reduced phosphorus is combined as ferrophosphorus and a small percentage remains in the slag in oxidized form.

The only two phosphorus blast furnaces of commercial size in the United States have been closed down and dismantled. This does not mean that the process is obsolete but is due largely to the favorable rates for hydro-electric power in certain localities that permit the economic operation of the electric furnace process.
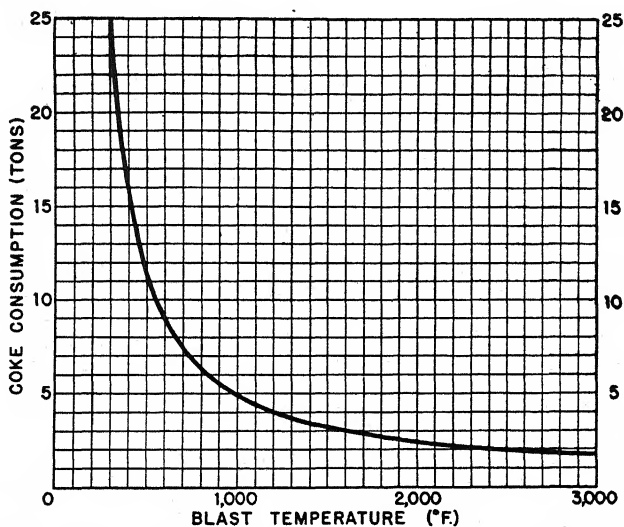
FIGURE 5. Effect of the air-blast temperature on the estimated amount of coke required per ton of P_2O_5 reduced in blast furnace smelting washed Florida land-pebble phosphate with a siliceous flux. Humidity, 0.01. (Heat losses taken into consideration.)

ELECTRIC FURNACE VERSUS BLAST FURNACE PROCESS FOR THE MANUFACTURE OF PHOSPHORUS

The choice between the electric furnace and blast furnace processes for the manufacture of elemental phosphorus depends on a number of factors, such as the size, cost and location of the plant and the availability and relative costs of coke and electric power as sources of thermal energy.

It is practicable to build a phosphorus blast furnace having fully twice the capacity of a single large electric furnace. On the other hand, such a blast furnace plant with its auxiliary equipment will cost about twice as much as two electric furnace plants having the same total capacity. Whereas, a large blast furnace will require less labor per ton of product than two electric furnaces, the yield of phosphorus from the former prob-

ably averages only 88 per cent, as against 92 per cent for an electric furnace plant.

A large blast furnace operates most economically at full capacity and its output cannot be curtailed without loss of efficiency. On the other hand, when market conditions are adverse, the production of an electric furnace plant consisting of two furnaces of equal size can be cut in half by closing down one unit without impairing the efficiency of the other.

Although coke as a source of thermal energy is available in many locali-
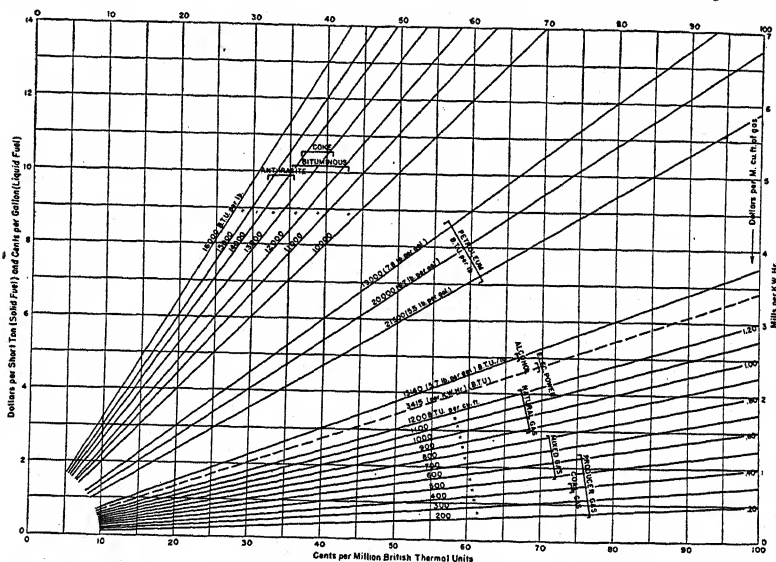
FIGURE 6. Comparative cost of million Btu's furnished by electric power and various types of solid, liquid and gaseous fuel.

ties at a much lower cost than electric power, hydroelectric developments in Alabama, Tennessee and in certain parts of the western phosphate fields have rendered electric power competitive with fuel in the manufacture of elemental phosphorus.

Unquestionably, the relative price of coke and electric energy is a major factor to be considered in making a choice between the blast furnace and electric furnace processes. Figure 6 gives diagramatically the cost of equivalent quantities of heat delivered by the combustion of various fuels compared with the cost of that derived from electric power.

It would appear off-hand that electric power as a source of thermal energy cannot compete with most of the fuels available in this country, but equivalent costs of the thermal unit furnished by electric power and fuel

by no means render these two processes economically equivalent. The heat derived from electric power is much more efficiently utilized since it is

TABLE 5. ESTIMATED COST OF PRODUCING ELEMENTAL PHOSPHORUS BY ELECTRIC-FURNACE METHOD

(Two electric furnaces; 330-day operation; annual production, 15,000 tons P equal to 33,000 tons P_2O_5)

Capital investment

Real estate	$ 10,000
Buildings	810,000
Equipment	2,551,000
Total	$3,371,000

	Unit Cost	Per Ton of Recovered Phosphorus[a]		Cost per Ton P_2O_5	% of Total Cost
		Quantity	Cost		
Raw materials					
Phosphate sinter (11.0% P), short ton	$5.45	9.88	$ 53.85	$23.51	35.22
Coke breeze, short ton	6.50[b]	1.40	9.10	3.97	5.95
Electrodes, Pounds	0.09	37.60	3.38	1.48	2.21
Electric energy, kw.-hr.	0.0025	13,200	33.00	14.41	22.23
Total for raw materials	...	...	$ 99.33	$43.37	65.61
Conversion					
Labor, operating and supervision			$ 10.39	$ 4.54	6.80
Labor, maintenance			8.69	3.79	5.68
Labor, laboratory and office			1.23	0.54	0.81
Power, other than furnace			0.34	0.15	0.22
Water and steam			1.74	0.76	1.13
General plant expense			1.19	0.52	0.80
Maintenance, materials			5.43	2.37	3.55
Depreciation (over-all), 7.5%			16.81	7.34	11.00
Insurance and taxes 3%			6.74	2.94	4.40
Total for conversion			$ 52.56	$22.95	34.39
Grand total			$151.89	$66.32	100.00

[a] Based on recovery of 92%.
[b] Coke breeze should be about 50 cents per ton less than lump coke.

localized within the furnace charge, is not dissipated in heating up large volumes of evolved gases, and there is far less loss from radiation than in the blast furnace process. On the other hand, the coke required for reduction and the electrode consumption in the electric furnace process must be added to the cost of the power requirements.

Tables 5 and 6 give the cost of producing elemental phosphorus by the

electric furnace and blast furnace processes at plants located in the western phosphate fields as estimated by Waggaman and Bell[31a]. These costs under the conditions assumed are more favorable to the electric furnace

TABLE 6. ESTIMATED COST OF PRODUCING ELEMENTAL PHOSPHORUS BY
BLAST-FURNACE METHOD

(Single furnace with annual production, 330-day operation, of 15,000 tons P equal
to 33,000 tons P_2O_5)

Capital investment

Real estate	$ 10,000
Buildings	250,000
Equipment	5,340,000
Total	$5,600,000

	Unit Cost	Per Ton of Recovered Phosphorus[a]		Cost per Ton of P_2O_5	% of Total Cost
		Quantity	Cost		
Raw materials					
Phosphate sinter (11% P), short ton..	$5.45	11.37	$ 61.97	$27.06	37.74
Coke (85% C), short ton...........	7.50	5.44	40.80	17.81	24.84
Total raw materials.............		16.31	$102.77	$44.87	62.58
Conversion					
Labor, operating and supervision[b]....			$ 6.92	$ 3.02	4.21
Labor, maintenance[b]...............			5.78	2.52	3.52
Labor, laboratory and office.........			1.23	0.54	0.75
Water and steam....................			1.74	0.76	1.06
General plant expense..............			1.19	0.52	0.73
Maintenance, materials.............			5.43	2.37	3.30
Depreciation (over-all), 7.5%........			27.95	12.21	17.03
Insurance and taxes 3%............			11.20	4.89	6.82
Total for conversion.............			$ 61.44	$26.83	37.42
Grand total.....................			$164.21	$71.70	100.00

[a] Based on recovery of 88% phosphorus.
[b] Labor, two-thirds that required for two electric furnaces.

process, but the location of the plant, fluctuations in the price of fuel and electric energy and slight variations in labor conditions and the cost of materials can change the economic picture.

WHITE PHOSPHORUS

Apart from its limited use in alloys such as phosphorus-copper, phosphorus-tin and phosphorus-bronzes, and its use in poisonous preparations

to control rodents and insect pests, white phosphorus has few industrial applications. In time of war, however, the demand for this element as an incendiary and for laying down smoke screens is very great and these direct military uses may call for many thousands of tons.

The chief phosphorus compounds, (other than phosphoric acid and its derivitives), which have important industrial uses are the sulfides and chlorides.

Phosphorus sesquisulfide (P_4S_3) is used extensively in the match industry, and phosphorus pentasulfide (P_4S_{10}) plays an important role in the manufacture of organic phosphorus-sulfur compounds that are added to lubricating oils to improve their resistance to oxidation and enable them to withstand high bearing pressures. Phosphorus pentachloride (PCl_5) is an effective reagent for converting alcohols and organic acids into their corresponding chlorides; phosphorus trichloride (PCl_3) and its derivative phosphorus oxychloride ($POCl_3$) are used in the manufacture of alkyl and aryl phosphates (see Chapter 25), and as reagents in the production of certain dye stuffs and drugs. The uses of phosphorus and its derivatives are shown diagramatically in Figure 7.

RED PHOSPHORUS

On heating liquid yellow phosphorus to a temperature slightly below its boiling point for a protracted period it is converted into an allotropic form of the element known as red phosphorus.

Pure red phosphorus, as its name implies, is a dark red solid that does not melt, and can be exposed to moderately high temperatures and oxidizing conditions without danger of spontaneous combustion. It can be readily handled and shipped.

Red phosphorus has a number of military and industrial applications but probably the largest proportion of that produced is used in the striking surface of safety match packages which consists of a mixture of red phosphorus, glue and powdered glass. When a match is drawn over such a coating, a minute but sufficient quantity of the red phosphorus is converted into the yellow variety to inflame the combustible match head. These matches are difficult to ignite by friction on any other type of surface and hence have greatly reduced fire hazards.

Until recently, the manufacture of red phosphorus has been a rather tedious and costly batch process consisting in heating the yellow phosphorus in a closed container at a temperature at 240°C or above for a period of 4 to 5 days. The product which consists largely of a cake of solid red phosphorus is then chipped out, ground under water and boiled in a solution of caustic soda to dissolve the unconverted yellow phosphorus.

Little or no improvement in this batch process was made for a period

of 50 years although a continuous process for the manufacture of red phosphorus was proposed and patented in Germany as far back as 1932[31].

There appears to be no record that such a scheme was actually developed
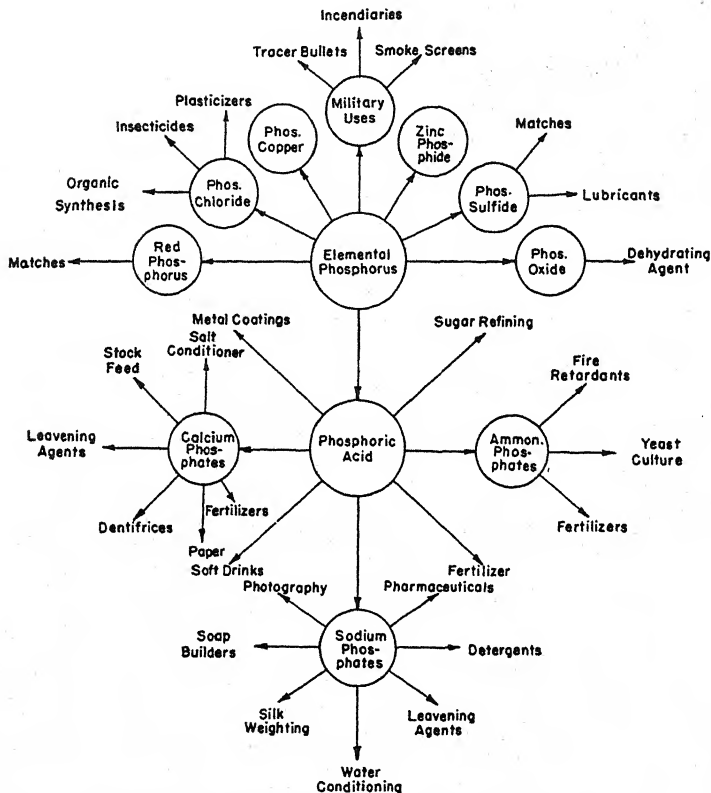
FIGURE 7. Phosphorus: some of its derivatives and uses.

until the Tennessee Valley Authority built and operated a pilot plant based on the results of certain investigations conducted by Dewitte and Skolnik[9] and Skolnik *et al.*[28] These experiments resulted in a process[8] for the continuous production of red phosphorus that saves both time and labor. Miller, Wilson and Tusson[16] have described this process and the equipment used in considerable detail but it may be briefly reviewed as follows:

The essential units consist of a feeder for introducing the yellow phosphorus into a steel reactor, 2 evaporators (in series) to volatilize unconverted, yellow phosphorus, a condenser for returning this yellow phosphorus to the system, means for introducing CO or other non-oxidizing gas into the system, a tank for wetting the red phosphorus discharged from the vaporizer and settling pan in which the final product (red phosphorus) is drained.

The yellow phosphorus is fed at a constant rate into the stainless steel reaction chamber which has a cone bottom and a gas-tight cover. The lower part of this reaction chamber is electrically heated and insulated to maintain a more or less constant temperature of 280°C. A vertical steel stirrer equipped with propellor blades extends through the top and well down into the cone of the reactor. An overflow pipe is provided just at the top level of the heating unit and the upper part of the reactor is water-cooled. The flow of yellow phosphorus is regulated so that it will be retained in the reactor for $4\frac{1}{2}$ to 5 hours. From the reactor, the slurry of yellow and red phosphorus overflows through a pipe into the first of 2 vaporizers connected in series.

These vaporizers consist of inclined stainless steel, covered troughs containing a screw conveyor for moving the slurry forward and are heated above the vaporization point of yellow phosphorus. As the material moves toward the exit of the first vaporizer much of the yellow phosphorus is distilled off and carried into a condenser along with the carbon monoxide gas which is introduced into the system countercurrent to the flow of the phosphorus slurry. The second vaporizer is heated to a somewhat higher temperature and serves to eliminate the residual yellow phosphorus still present in the red phosphorus. Breaker-plates in the second vaporizer disintegrate any lumps of red phosphorus and facilitate its purification.

From the second vaporizer the finely divided red phosphorus is discharged into a tank where it is stirred with water, washed free of soluble impurities and the suspension passed to a settling tank where it is allowed to drain. Finally the damp product is dried at 150°F for 12 to 24 hours. An alternate method not fully developed provides for handling the red phosphorus from the vaporizers without the use of water.

In addition to traces of unconverted yellow phosphorus, the presence of certain metallic impurities in red phosphorus cause it to oxidize even at ordinary temperatures. This tendency to oxidize not only involves the risk of spontaneous combustion, but gives rise to the formation of certain corrosive and poisonous products.

Silverstein *et al.*[27] studied the effects of a number of inorganic and organic substances on the oxidation rate of red phosphorus. These investigators found that while such metals as bismuth, copper, silver, iron, nickel,

cadmium, lead, chromium and tin accelerated the oxidation of red phosphorus, alumimum and zinc acted as retarders. Moreover, the addition of small quantities·of the oxides of these latter two metals stabilized the red phosphorus still further.

Iron and copper are the two metallic impurities most likely to be present in commercial red phosphorus. By treating the product with sulfuric acid most of the iron can be leached out, but the copper is best removed by dissolving it with cyanide solution.

According to the above investigators red phosphorus substantially free from copper and iron, when lightly coated with aluminum hydroxide can be kept almost indefinitely without deterioration.

The great reduction in fire hazards resulting from the shipment of phosphorus in a form not spontaneously combustible opens up interesting possibilities. If a freight rate for such material were established commensurate with that for sulfur, the distance that phosphorus could be economically shipped should be greatly extended. The saving in transportation charges thus effected would warrant substantial investments in facilities for converting white phosphorus into the red variety at points of production.

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11. Manufacture of Phosphoric Acid from Elemental Phosphorus

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INTRODUCTION

Whereas most of the orthophosphoric acid for industrial purposes was, and probably still is produced by the sulfuric acid or so-called wet process, the manufacture of this acid from elemental phosphorus is by no means new. For many years appreciable quantities of pure concentrated phosphoric acid for technical and medicinal use have been derived directly from the oxidation of phosphorus and the hydration of the resultant P_2O_5.

As mentioned in the previous chapter, however, this process began to assume great commercial significance after the pioneer work conducted by the Bureau of Soils, U. S. Department of Agriculture, between 1918 and 1922.[2, 12, 17, 18].

Based on the results obtained in these pilot plant experiments, electric furnaces of commercial size were built and operated successfully by the Federal Phosphorus Company at Anniston, Alabama[15], and later, phosphorus blast furnaces were erected and operated by the Victor Chemical Works at Nashville, Tennessee[7], and by the Coronet Phosphate Company at Pembroke, Florida[16].

In 1934 the Tennessee Valley Authority began a systematic study of various types of equipment and operating procedures for producing and recovering phosphoric acid. This government agency, the Monsanto Chemical Co., and the Victor Chemical Works are largely responsible for developing and improving the general process that now is so successfully employed[1, 3, 4, 5, 6, 11, 14].

Whether the electric furnace or blast furnace is employed in the manufacture of phosphoric acid, the fundamental reactions involved are the same and comprise first the reduction of phosphate rock to white phosphorus as already described, followed by oxidation of this element and hydration of the resultant P_2O_5 as shown in the following two equations:

$$P_4 + 5O_2 \rightarrow 2P_2O_5 \tag{1}$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4 \tag{2}$$

The manner in which the phosphorus is oxidized, however, represents the difference between the so-called one-step and two-step modifications of this general method.

THE ONE-STEP PROCESS

The one-step process, as its name implies, consists in producing phosphoric acid in a single continuous operation, thus obviating the necessity of using phosphorus condensers.

The volatile products from the electric or blast furnace after being freed from dust, (as described in the previous chapter), pass directly to a suitable combustion chamber. Here the phosphorus vapor and carbon monoxide gas are either burned simultaneously, or the phosphorus is selectively oxidized (as described later) leaving the bulk of the carbon monoxide unburned for subsequent use.

In any event, the fully or partially oxidized products are cooled, hydrated and then passed through suitable absorption towers or a Cottrell electrical precipitator for the recovery of the phosphoric acid. The Cottrell precipitator is generally favored for collecting the final product.

Handling Electric Furnace Gas

The following is a description of the phosphoric acid plant #2 of the Tennessee Valley Authority and the method of operating it when employing the one-step process. Numerous changes were made in this plant since it was first constructed in 1934, but the size of the combustion chamber and basic principles of operation were not materially altered until it was closed down in May 1944[14].

Combustion Chamber. The combustion chamber of this plant burned 1,100 pounds of phosphorus and 3,080 pounds (39,500 cu ft at STP) of carbon monoxide per hour, employing a volume of air 50 per cent in excess of that theoretically required to fully oxidize these furnace products. The inside of this chamber was 35'4" long, 12'0" high (from the lowest part of the hearth to the roof) and 8'9" wide.

The hearth was lined with carbon blocks and the walls with $15\frac{1}{2}$ inches of firebrick. In order to cool the gases of combustion, 90 cast iron tubes, through which water circulated, lined the side walls of the combustion chamber. Additional pipes were suspended from the roof of the chamber so that the gas in leaving the chamber passed through a bank of water-cooled tubes.

The furnace gases (at temperatures ranging from 950 to 1300°F) entered one end of the combustion chamber through a brick-lined main (2'0" inside diameter), and were mixed with air introduced through 8 ports surrounding the gas inlet. The gaseous products of combustion, after contact

with the tubes through which the cooling water was circulated, passed out of the combustion chamber at 1250 to 1500°F. These cooling tubes carried away from 35 to 45 per cent of the heat liberated by the oxidation of the phosphorus and furnace gas.

The gases and oxidized phosphorus left the top of the combustion chamber through a brick-lined main (2′6″ inside diameter) where they were sprayed with water at the rate of 5 gallons per minute and the temperature reduced to 600°F before they entered the hydrator.

Hydrator. This unit consisted of an unpacked cylindrical chamber 34 feet high and 10 feet in diameter (inside) lined with $13\frac{1}{2}$ inches of acid-proof brick. The dished bottom was of acid-proof brick set in a lead pan. A carbon tube in the center of the bottom served to drain the acid produced into a gas-sealed receptacle from which it overflowed into a storage tank. The gases entered the top of this hydrator and were sprayed with additional water at the rate of 10 gallons per minute which reduced the temperature to about 250°F. They left the hydrator through a stainless steel flue (3′6″ in diameter) near the base of the chamber and entered the electrical precipitator at a temperature of 225°F. Approximately 1,800 pounds of phosphoric acid per hour, or about 40 per cent of that produced, was collected in the hydrator at a concentration of 80 per cent H_3PO_4.

Cottrell Precipitator. The Cottrell electrical precipitator consisted of three sections connected to the gas flue from the hydrator by means of a manifold. Each section contained 36 vertical carbon tubes (collecting electrodes) 10 inches in diameter and 12 feet in length enclosed in a brick chamber. The discharge electrodes consisted of single stainless steel wires hung from an insulated frame down the center of each tube. The lower end of each wire was fastened to a stainless steel grid to prevent individual swaying of these electrodes. The precipitator was operated at 40,000 volts and the current consumption was approximately $\frac{1}{8}$ kva per 1,000 cubic feet of gas treated.

The gases from the hydrator passed through the manifold and entered each section of the precipitator through a 2′6″ flue midway in the side of the brick housing and were drawn downward in this header and then up through the carbon tubes wherein the balance of the P_2O_5 was precipitated in the form of concentrated H_3PO_4 at the rate of 2,600 pounds per hour. The residual gases were then drawn from the upper headers of the precipitators by means of exhaust fans and discharged into the atmosphere through a brick stack. The acid drained from the precipitator through an acid-proof trough to a tank from which it was pumped to storage.

A flow diagram of this plant operating on the one-step principle is shown in Figure 1, and the construction of the combustion chamber for burning the gas and phosphorus direct from the electric furnace is shown in Figure 2.
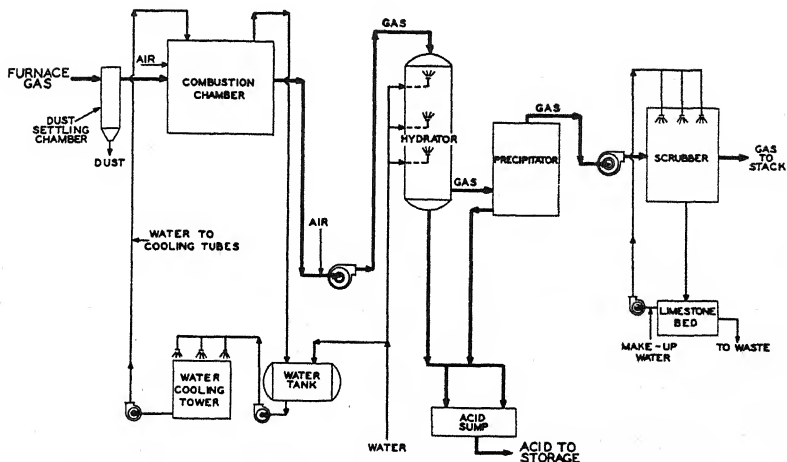
FIGURE 1. Flow diagram of Acid Plant No. 2 for burning electric-furnace gas.
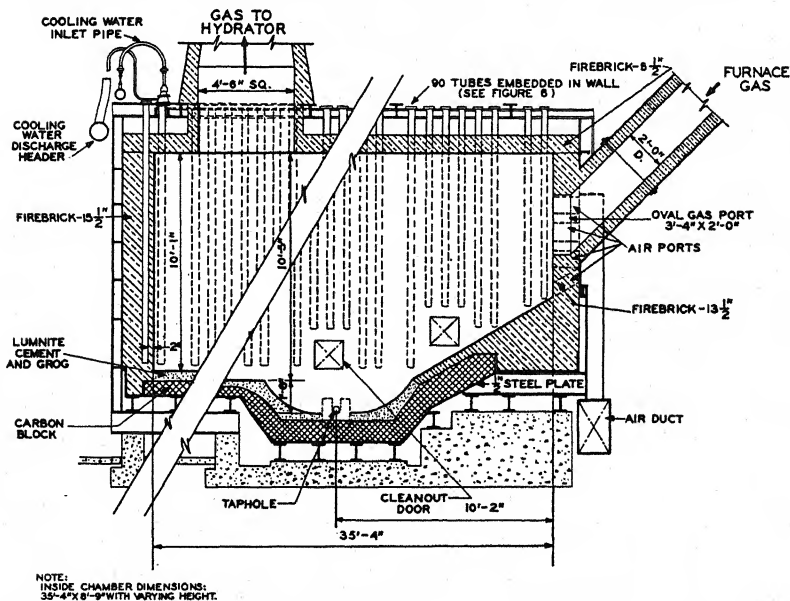
(*Courtesy of TVA*)

FIGURE 2. Final combustion chamber of Acid Plant No. 2 for burning electric-furnace gas.

Advantages and Disadvantages of One-Step Method

Theoretically, the one-step process is the simplest, and should be the most economical method of producing phosphoric acid since it eliminates a somewhat elaborate and costly condensing system, obviates the necessity of providing phosphorus storage facilities, and renders unnecessary the steam jacketed pipe lines and extra pumps for rehandling liquid phosphorus and recirculating condensing water.

Up to the present time, however, the one-step process has shown certain disadvantages that more than offset the advantages mentioned above. These disadvantages may be listed as follows:

(1) The one-step process entails the use of larger equipment for the combustion of the phosphorus and the collection of the resultant phosphoric acid because of the greater volume of the gases relatively dilute with respect to P_2O_5.

(2) The thermal value of the gases (other than phosphorus vapor) cannot be efficiently utilized because of the scorifying and corrosive nature of the P_2O_5 contained in the products of combustion. This is particularly serious if the blast furnace is used since it is essential to preheat the air blast to a high temperature for economical operation.

(3) The immense number of thermal units released by the complete oxidation of both phosphorus and carbon monoxide necessitates the use of elaborate cooling devices in the combustion chamber to prevent the rapid deterioration of this unit and to insure that the gases pass to the phosphoric acid collecting system at a temperature and velocity permitting the complete recovery of the P_2O_5.

(4) The direct combustion of phosphorus vapor containing volatile contaminants derived from the phosphate rock produces crude phosphoric acid that must be purified before it is suitable for use in the manufacture of food and chemical grade products.

(5) The immense volumes of air (carrying an appreciable percentage of moisture) cause the formation of substantial amounts of metaphosphoric acid in the combustion chamber or heat regenerative equipment (hot blast stoves). Metaphosphoric acid at high temperatures is a thick viscous slag-like liquid that attacks siliceous refractories and hence yields impure orthophosphoric acid when it is subsequently hydrated.

Handling Gas from the Phosphorus-Blast Furnace

Since the heat required for smelting phosphate rock in the blast furnace is derived from the combustion of coke in direct contact with the phosphate charge, the volume of gases evolved per unit of phosphorus volatilized is many times greater than that from an electric furnace having the same rated capacity.

Repeated tests have shown that the gas from the electric furnace contains from 7 to 7.4 per cent phosphorus, whereas the gas from the blast furnace averages only 1.0 per cent of this element. In other words, a phosphorus blast furnace emits from 7 to 7.4 times more gas for each pound of phosphorus volatilized.

Moreover, while the concentration of carbon monoxide in blast furnace gas is only about 40 per cent as great as in electric furnace gas, due to the nitrogen contained therein, the actual quantity of CO evolved from the blast furnace per unit of phosphorus is twice as great.

It is obvious, therefore, that in order to burn this greater volume of gas and handle the oxidation products, a much larger combustion chamber is required, additional cooling facilities must be provided and larger collecting units installed to insure the complete recovery of the P_2O_5 in the form of concentrated phosphoric acid.

Finally, the economic efficiency of the phosphorus blast furnace depends upon the utilization of the thermal value in the gas to heat the air required for the combustion of the coke and to generate power for the operation of the plant. The burning of gas containing phosphorus in hot blast stoves and under boilers is not practical because of the scorifying and corrosive action of the P_2O_5 and H_3PO_4 produced in highly heated siliceous refractories and exposed metal parts.

Therefore, until the preferential oxidation of the phosphorus in furnace gas is successfully and fully developed, the one-step process for the manufacture of phosphoric acid through the medium of the blast furnace is not very attractive.

Preferential Oxidation of Phosphorus

The one-step process, however, is by no means obsolete, particularly since the TVA has shown that the phosphorus vapor in the gases from either the electric or blast furnace can be preferentially oxidized to P_2O_5, leaving the bulk of the carbon monoxide available for fuel purposes[9, 14].

In order to determine the applicability of preferential phosphorus oxidation to the electric furnace process, experiments were conducted in which phosphorus was vaporized and mixed with electric furnace gas in the proportion and at the temperature (600°F) that these are normally evolved from the electric furnace. This gaseous mixture was then passed to a preferential oxidation chamber where air was supplied at a rate somewhat in excess of that theoretically required to fully oxidize the phosphorus. The temperature of the oxidation chamber was controlled by the introduction of water in the form of spray and the phosphoric acid produced was collected in a packed tower followed by a cooler. By keeping the temperature of the oxidation chamber between 850 and 1000°F with an air input be-

tween 120 and 130 per cent of that theoretically required for the combustion of the phosphorus, it was found that the latter was fully oxidized to P_2O_5; but only from 5.6 to 7 per cent of the carbon monoxide was oxidized.

Similar experiments were conducted by Hignett[9] with gas of the composition normally evolved from the phosphorus blast furnace and equally good results obtained.

Figures 3 and 4, taken from the report of TVA, show the percentage of oxidation of phosphorus and carbon monoxide in electric furnace and blast furnace gas respectively where an appreciable excess of air (both dry and humid) over that theoretically required for the combustion of phosphorus is employed.

Whereas the preferential oxidation of phosphorus in either electric or blast furnace gas has not been developed beyond the pilot plant stage, the results indicate that it can be employed on a commercial scale. If so, many of the objectionable features previously encountered in the operation of the one-step process for the production of phosphoric acid of a grade suitable for fertilizer use should be eliminated. The acid manufactured in this way however will require purification if it is to be employed in the manufacture of high grade phosphate chemicals and food products.

THE TWO-STEP PROCESS

The two-step process for the manufacture of phosphoric acid derives its name from the fact that it involves two distinct operations. It is applicable to either electric furnace or blast furnace gas, but so far has been chiefly used for treating the former.

In general the process consists in separating the dust from the volatile products of the furnace, condensing the phosphorus as a mobile liquid and utilizing the non-corrosive combustible gas (largely carbon monoxide) for fuel purposes. The recovered phosphorus is stored, subsequently burned in a separate combustion chamber and the resultant P_2O_5 hydrated and collected in the manner described Chapter 10. Since the phosphoric acid plant is not directly connected with the phosphorus furnace, it is operated as a separate unit and hence can be shut down without interfering with furnace operations.

Although the one-step process was used on a large commercial scale for more than a decade before the two-step process was extensively developed, the latter is now more widely used. This change-over has been due to a number of reasons that are enumerated on pages 168 and 171.

The following description of the equipment and operation of a phosphoric acid plant designed to burn 2,000 pounds of liquid phosphorus per hour is based on a staff report of the Tennessee Valley Authority compiled by Striplin[11]. The various units of this plant and the operating details are

AIR INPUT: 120-130 % THEORETICAL FOR P₄O₁₀ FORMATION.
PHOSPHORUS RATE: 0.29 LB./ (HR) (CU. FT. COMBUSTION SPACE.)
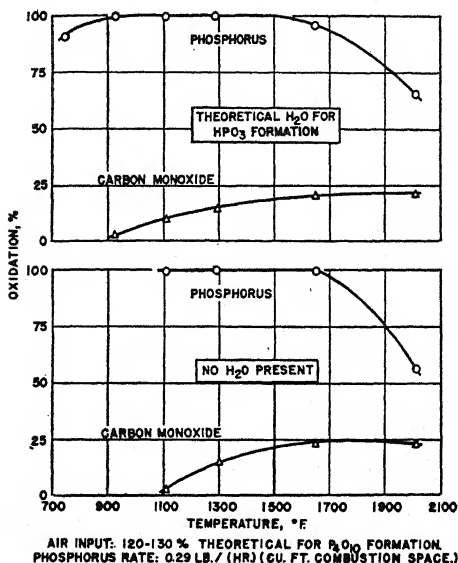
FIGURE 3. Oxidation of phosphorus and carbon monoxide in small-scale preferential oxidation tests with simulated electric-furnace gas.

AIR INPUT: 140-200% THEORETICAL FOR P₄O₁₀ FORMATION.
PHOSPHORUS RATE: 0.27-0.36 LB./ (HR) (CU. FT. COMBUSTION SPACE.
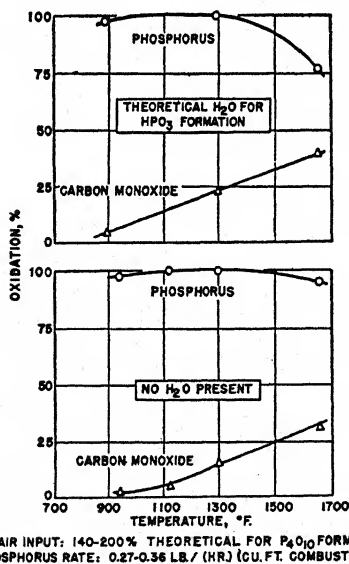
FIGURE 4. Oxidation of phosphorus and carbon monoxide in small-scale preferential oxidation tests with simulated blast-furnace gas.

substantially the same whether the phosphorus is reduced from phosphate rock smelted either in an electric or blast furnace.

Phosphorus Feeding and Metering Equipment

The phosphorus metering system for this plant is automatically controlled and buoyancy-type level indicators are used. Two tanks (each having a capacity of 150,000 pounds of elemental phosphorus) are used alternately as phosphorus reservoirs from which the phosphorus is discharged into the combustion chamber by displacement with water.

Hot water for this purpose is supplied from a third tank by means of a centrifugal pump. This pump, which is equipped with a by-pass containing a relief valve (in the event the system becomes clogged), delivers water under a pressure of 25 psi. All the tanks are provided with submerged steam coils to keep the water and phosphorus at a temperature above the melting point of the latter (60°C).

When it is desired to refill a tank with phosphorus, the water employed in displacing this element is returned to the hot water tank and used over again, precautions being taken to settle out suspended phosphorus. Any acidity that develops in this water is neutralized with soda ash. A separate hot water tank and pump are provided for the water jacket surrounding the phosphorus pipeline leading to the combustion chamber.

Combustion Chamber. The phosphorus is sprayed into the top of the combustion chamber by means of compressed air (under a pressure of 25 psi) through a special type of burner. The tip of this burner is water-cooled to protect it from the high temperatures developed in the combustion chamber. Secondary air for full oxidation of the phosphorus is supplied from a windbox (surrounding the burner) at the rate of 5,000 cubic feet per minute. A photograph of the burner and its arrangement is shown in Figure 5.

The phosphorus combustion chamber itself is a relatively new development designed to reduce depreciation and cost of replacements and produce a purer acid than heretofore obtained. Graphite is the main structural material used and no steel shell or outer casing subject to corrosion is used.

This combustion chamber is 35 feet in height, with an inside diameter of 14½ feet. The bottom and walls are constructed of specially cut graphite blocks set in asphalt cement. This structure is supported about 11 feet above ground level in order to permit any metaphosphoric acid formed in the bottom of the chamber to drain into the upper part of the gas cooler immediately following this unit. The graphite blocks forming the bottom of the combustion chamber are laid in a pan of stainless steel (5 inches deep) to prevent loss of metaphosphoric acid through seepage. The dome-like steel top of the combustion chamber is lined with 9 inches of acid-resisting grog and cement.

Facilities are provided to supply cooling water at the rate of 1,500 gallons per minute to the exterior surface of the graphite walls by means of a spray ring around the dome of the combustion chamber. This water runs down the walls as a film but is deflected near the base of the tower to prevent it from entering any cracks that may open up in the bottom of the chamber during operations. The walls of the combustion chamber are thus maintained at temperatures ranging from 80 and 125°C.

In order to lower the temperature of the P_2O_5 and reduce the volume of gas, a special type of cooler is installed between the combustion chamber
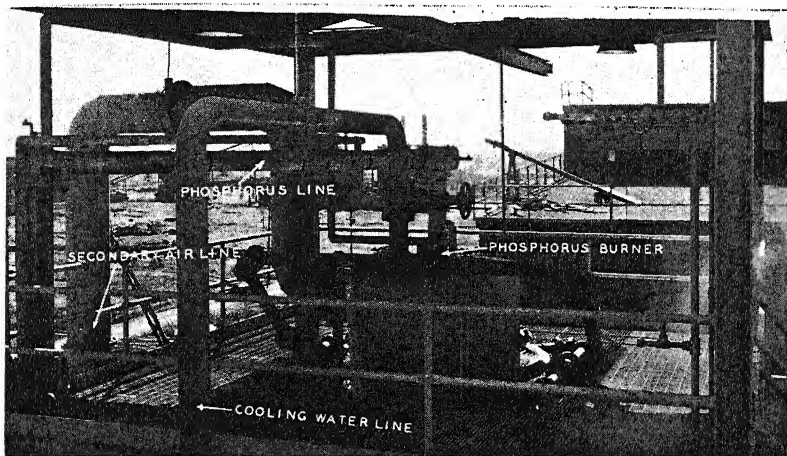
(Courtesy of TVA)

FIGURE 5. Phosphorus burner and top of graphite combustion chamber of acid plant No. 2M.

and the hydrator. This cooling chamber is also constructed of carbon slabs and contains 150 horizontal graphite tubes having an inside diameter of 3 inches through which cold water is introduced; the rate at which the water is circulated is automatically adjusted by the temperature at which it passes out of the cooling system. Additional water is sprayed on the outside of the cooling chamber to keep the temperature of the graphite walls sufficiently low to prevent oxidation.

The gas from the combustion chamber enters the cooler (at a temperature of 1450°F) through a water-cooled duct (3′4″ diameter) and leaves at a temperature of 350°F through a graphite lined steel flue (2′9″ inside diameter). It then enters the side of the hydrator near its base.

The Hydrator. This unit consists of an acid-proof brick chamber lined with $4\frac{1}{2}$ inches of carbon brick and has a dome-like acid-proof top. No

an inside diameter of 7 feet, 11 inches. Three rows of spray nozzles (6 nozzles to each row) discharge water into the hydrator at the rate of 18 gallons per minute. These sprays not only provide enough water to fully hydrate the P_2O_5 to H_3PO_4, but also serve to reduce the temperature of the gas to less than 212°F. Approximately 55 per cent of the P_2O_5 in the gas is collected by this hydrator as phosphoric acid having a concentration of 75 to 95 per cent H_3PO_4. The gas containing the balance of the P_2O_5 and acid spray leave the hydrator through a graphite-lined steel duct

A - Phosphorus Storage Tank
B - Phosphorus Burner (Not visible)
C - Secondary Air Duct
D - Combustion Chamber
E - Hydrator
F - Electrostatic Precipitator
G - Acid Sump
H - Stack
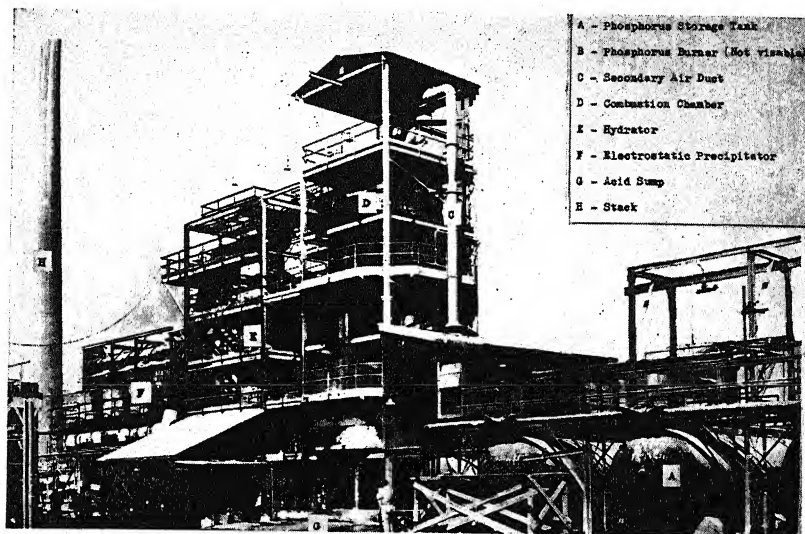
(Courtesy of the TVA)

FIGURE 6. Phosphorus combustion chamber and auxiliary equipment for the recovery of phosphoric acid.

(2′9″ inside diameter) and enter the lower headers of 3 precipitator units (connected in parallel) of the type previously described wherein the remaining P_2O_5 (40 per cent or more) is collected as strong phosphoric acid.

The arrangement of this plant for manufacturing phosphoric acid by the two-step process is shown in Figure 7.

Advantages of the Two-Step Process

The general adoption of the two-step process for manufacturing phosphoric acid by the thermal reduction of phosphate rock is due to the following factors:

(1) It has overcome certain operating difficulties inherent to the one-step process.
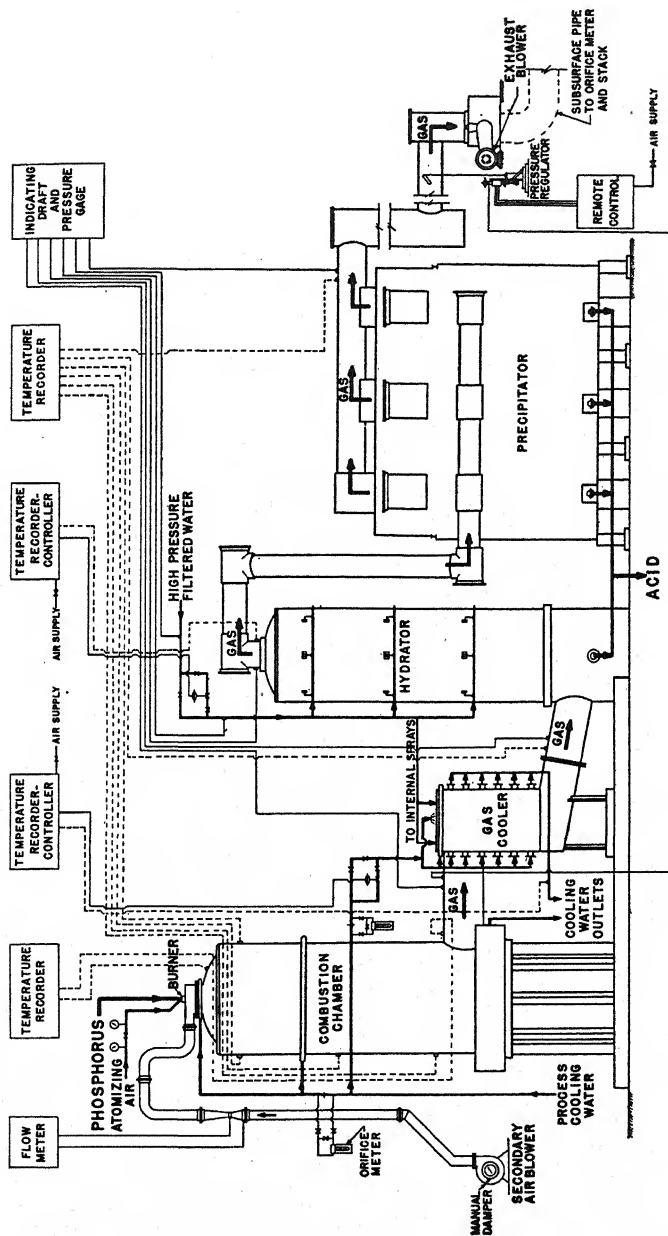
FIGURE 7. General arrangement and instrumentation of Acid Plant No. 2M for producing phosphoric acid from elemental phosphorus by the two-step process.

(*Courtesy of the TVA*)
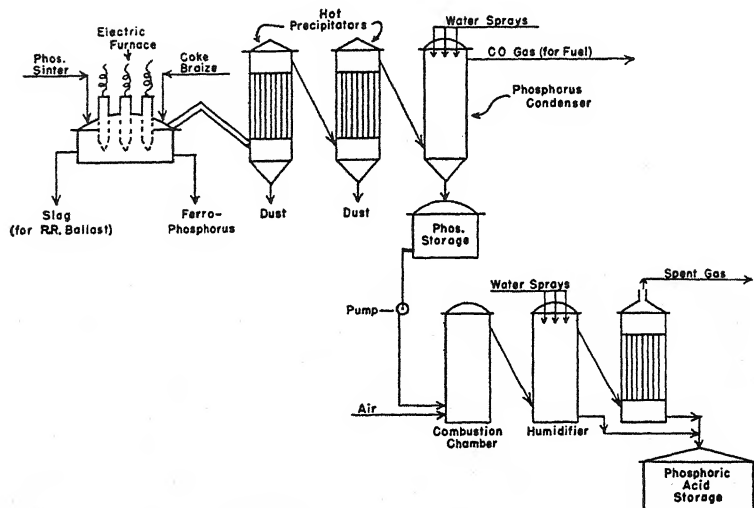
FIGURE 8. Flow sheet of two-step process for manufacturing phosphoric acid by the electric furnace method.
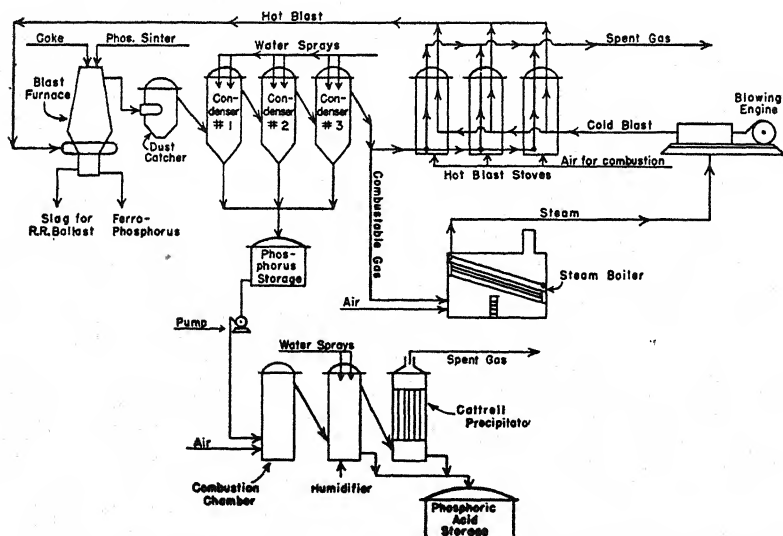
FIGURE 9. Flow sheet of the two-step process of manufacturing phosphoric acid by the blast furnace method.

(2) It has made possible the manufacture of a highly concentrated acid requiring a minimum amount of purification.

(3) Its flexibility is such that it is possible to supply either phosphoric

acid for industrial purposes or elemental phosphorus to meet military needs.

(4) It permits the efficient use of the carbon monoxide gas obtained as a by-product.

(5) The capital investment and depreciation on the phosphorus combustion chamber and acid recovery system is considerably less than in the one-step process.

Flow sheets of the two-step process for the manufacture of phosphoric acid by the electric furnace and blast furnace methods are given in Figures 8 and 9.

SIMULTANEOUS PRODUCTION OF PHOSPHORIC ACID AND HYDROGEN

A novel method of treating the gases evolved in the thermal reduction of phosphate rock involves the simultaneous manufacture of phosphoric acid and hydrogen. This process was originally proposed by Liljenroth[10] about 25 years ago, and is based on the reaction between phosphorus vapor and steam at elevated temperatures (by the aid of a suitable catalyst) as shown in the following equation:

$$P_4 + 10H_2O \rightarrow 2P_2O_5 + 10H_2$$
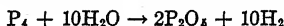
In the presence of an excess of steam the P_2O_5 is converted into phosphoric acid and removed either in an absorption tower or by electrical precipitation; hydrogen is recovered as a by-product.

Liljenroth's original patent covers the direct treatment of the volatile products (CO and P) with steam as they are evolved from the electric furnace and since this does not entail the preliminary step of condensing elemental phosphorus, it may be regarded as a modification of the one-step process. The inventor claims that all of the phosphorus vapor and part of the carbon monoxide are oxidized and the resultant P_2O_5 is hydrated by the excess of steam to form phosphoric acid. If desired, the residual or unoxidized CO may be converted into hydrogen and CO_2 by further reaction with steam.

The two subsequent patents of this inventor are for the oxidation of phosphorus alone and hence are adapted to the manufacture of phosphoric acid by the two-step process. These patents comprise the feeding of one volume of phosphorus vapor and 20 to 60 volumes of steam (at a temperature of 500 to 600°C) over or through a palladium asbestos catalyst at a rate corresponding to the production of 50 liters of hydrogen per hour per gram of palladium in the catalyst chamber.

Theoretically this process offers two outstanding advantages:

(1) It utilizes part of the heat energy released in the oxidation of phosphorus which in the present phosphoric acid processes is largely dissipated.

(2) It offers a means of obtaining hydrogen as a by-product which can be used in the manufacture of synthetic ammonia, a compound that fits in well with an intergrated program for producing concentrated fertilizers containing both nitrogen and phosphoric acid.

So far this process has not been practiced commercially but laboratory investigations recently reported by Schultz *et al.*[13] and subsequent pilot plant experiments conducted by Hein and his co-workers[8] of the TVA appear to have solved some of the equipment and engineering problems and point the way to the further development of this process.

In the laboratory experiments referred to above the efficiency of various types of metallic catalysts supported on a phosphate base were compared, but in protracted tests, only those catalytic bases consisting of aluminum, titanium and zirconium phosphates proved sufficiently resistant to the high temperatures and corrosion conditions imposed upon them.

The active ingredients of the catalytic bodies tested consisted of platinum, palladium, silver and copper. All of these were quite effective, but platinum and palladium were the most stable. Whereas there was a gradual loss of metal and a falling off in the efficiency of the copper catalyst, the low cost of this metal offers economic advantages where provision is made to renew the copper.

In the pilot plant work conducted by Hein and his co-workers[8], somewhat higher temperatures (700 to 800°C) were employed in the catalytic chamber than specified by Liljenroth and a steam-phosphorus molecular ratio of 18 to 1 was maintained. After passing through the catalytic body the volatile products entered a so-called convertor wherein oxidation of the phosphorus was completed and most of the phosphoric acid collected.

A materials balance based on the operation of this plant showed that 93.8 per cent of the total phosphorus introduced was converted into phosphoric acid, 2.7 per cent was evolved as phosphine (PH_3), 1 per cent was collected as elemental phosphorus and 2.5 per cent was unaccounted for. The off gas contained 99.8 per cent of hydrogen.

A list of U. S. patents dealing with the oxidation of phosphorus is given in Table 15 of the Appendix.

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12. The Manufacture of Phosphoric Acid by the Wet Process

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INTRODUCTION

The production of orthophosphoric acid on a large scale by the sulfuric acid process was originally undertaken with a view to utilizing lower grades of phosphate rock which yielded only relatively dilute superphosphate (12 to 14 per cent P_2O_5). The plan suggested was to treat such phosphates with sufficient sulfuric acid to convert completely their P_2O_5 content into orthophosphoric acid, filter off the insoluble residue, evaporate the phosphoric acid and use this strong acid solution to treat a second batch of phosphate rock, thereby producing the concentrated fertilizer material commonly known as triple superphosphate, the manufacture of which is described in Chapter 16.

When the higher grade phosphate deposits of the United States were discovered, the preparation of phosphoric acid as an intermediate product in the manufacture of phosphatic fertilizers was no longer essential, but as the economic advantages of concentrated fertilizer products became apparent, the manufacture of phosphoric acid either by the so-called wet process or by thermal reduction methods assumed increasing importance. Such concentrated fertilizers can only be produced through the medium of phosphorus or phosphoric acid.

In addition to its use for the prime purpose of making fertilizers and phosphate salts there appears to be an increasing probability that phosphoric acid may be used as a reagent in certain industrial processes instead of sulfuric acid, thus obtaining products or by-products of commercial value.

SOURCE OF PHOSPHATE

The basic raw material for the production of phosphoric acid may be either bones or certain natural minerals. Bones, when used, must be degreased and calcined. They represent a high-grade raw material and, therefore, are used principally as a source of phosphoric acid for chemical

production and, to a rapidly decreasing extent, for fertilizers, either directly or as a precipitated product.

The sources and characteristics of the mineral phosphates are described in detail in Chapters 4 through 9. The most desirable grade of rock to use when producing phosphoric acid for fertilizer purposes is dependent mainly on transportation costs and usually is that grade which can be delivered at the least cost per unit of P_2O_5. Most impurities, within the limits encountered in average commercial grades of rock, do not seriously affect the processing. Excessive organic material as found in some of the North African and western rocks can be troublesome, causing foaming, dirty acid and filter cloth blinding. Resort is often made to calcination of the rock to burn off the organics. In the case of phosphoric acid used for the production of chemicals and food products, calcination of the rock is often desirable from the standpoint of improving the color of the resulting product. Also, the iron and aluminum impurities should be at a minimum since they consume P_2O_5 in the subsequent purification steps. For the wet process, it is obviously desirable to keep the calcium carbonate at a minimum since this consumes acid without any compensating conversion of P_2O_5. The Tunisian and Algerian rocks are at a disadvantage in this respect. Fluorine is an objectionable impurity, but in all deposits except the Island rocks and bones the $F:P_2O_5$ ratio is surprisingly constant for any particular region[31]. Flotation, if used in beneficiating the rock, often leaves flotation oils in the concentrate, which can cause persistent foaming in the phosphoric acid plant similar to that encountered with high organic rocks. It can be seen that the pedigree of the available phosphate rocks, as well as their cost, must be studied carefully in determining their suitability for the production of phosphoric acid.

TYPE OF ACID

Whereas phosphoric acid may be produced by the action of either hydrochloric acid or nitric acid on natural phosphates, the soluble nature of the salts contained in the resulting products is such as to make the separation of the phosphoric acid difficult or commercially impracticable (see Chapter 18).

On the other hand, the main products obtained when phosphate rock is treated with sulfuric acid are phosphoric acid and gypsum. The latter being a relatively insoluble compound can be readily separated from the acid by filtration. Therefore, from a practical standpoint, sulfuric acid is the only inorganic acid considered commercially applicable to the manufacture of phosphoric acid by the so-called wet process.

The sulfuric acid employed for the production of phosphoric acid may be derived from either the lead chamber or the contact type of plant. The

strength is not material except that the stronger the acid the more concentrated is the phosphoric acid produced therefrom, hence where readily available, 66° Bé acid is to be preferred. Attempts have been made to use waste sulfuric acid such as that obtained from petroleum alkylation plants, but any appreciable quantities of organic impurities introduce serious complications in the manufacture of phosphoric acid from these wastes.
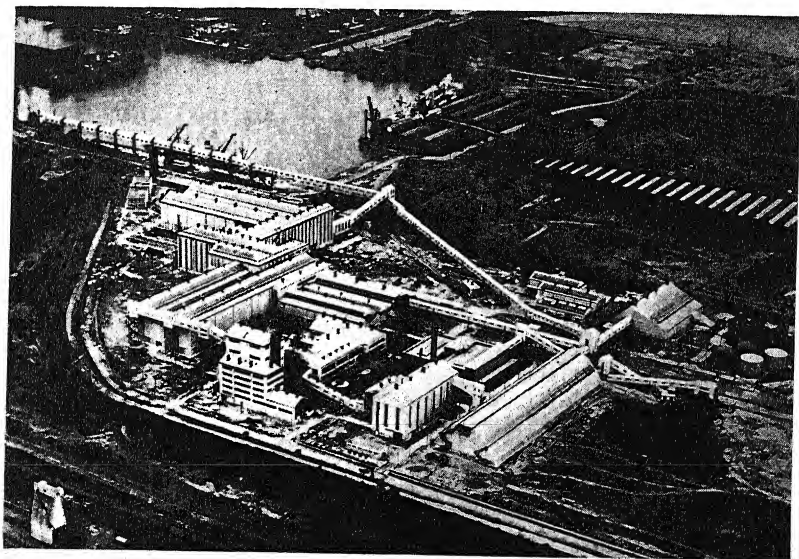
FIGURE 1. General view of a modern plant for producing phosphoric acid and triple superphosphate by the wet process at Immingham, England.

HISTORY OF DEVELOPMENTS

In the early days, small quantities of phosphoric acid were produced by leaching superphosphate with a weak sulfuric acid, but this was later abandoned in favor of the direct production of phosphoric acid from phosphate rock or bones. Older plants agitated phosphate rock with 30 to 40 per cent sulfuric acid in batch tanks and then separated the phosphoric acid from the gypsum on filter beds or in filter presses. The main disadvantages of the old process aside from high labor requirements were that the filter beds or presses became clogged, filtration was slow, excessive quantities of water were used to wash the residue, and the filters had to be continually cleaned and frequently repaired because of the extremely corrosive nature of the acid.

The first and probably most important attempt to modernize the chemi-

cal engineering application of this process, and to make it feasible for quantity production, was by the application of continuous countercurrent decantation using Dorr thickeners for washing the gypsum. Almost simultaneously, the reaction was made continuous by the use of the Dorr-type of airlift agitator, and it is this system of continuous agitation and continuous decantation which has come to be known as the Dorr System and which is amply described in some of the older textbooks and in the litera-
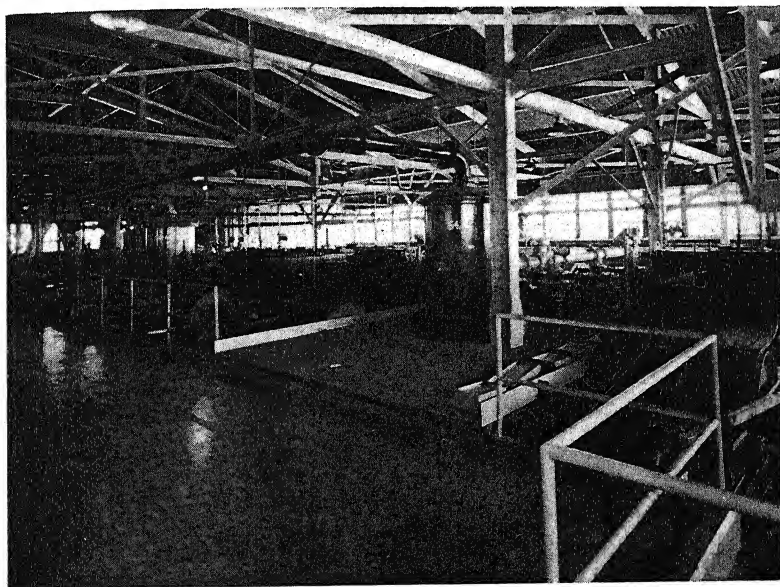
FIGURE 2. Interior view of a modern plant producing phosphoric acid by the sulfuric acid process.

ture[11, 16, 30, 37]. Over 25 plants of this type were built during the period 1917 to 1929. During this time the system underwent a considerable evolution. Whereas, in the earlier plants, countercurrent decantation alone was depended upon to remove the acid from the gypsum (using 5 or 6 thickeners in series), it was found that, as adequate acid-resisting, continuous filtration equipment was developed, better results could be obtained by 3 or 4 thickeners followed by a drum filter. Experience also showed that results could be improved by more intensive agitation than was obtainable in air agitators, and a special design of mechanical agitator was gradually evolved. During this period the idea of grinding the phosphate rock wet in specially designed acid-resisting pebble mills, using phosphoric acid as a

grinding solution, was developed and very generally adopted[10, 33]. A few plants used classifiers in closed circuit with the mills. The maximum strength of acid obtainable with this countercurrent decantation method of washing was around 20 to 22 per cent P_2O_5. The recoveries were high and the labor requirements low, but the plant costs were considerable due to the large equipment and the tremendous amount of lead and building required. Attempts were made to increase the strength of the acid and to obtain rapidly settling gypsum so that the size of the thickeners could be materially reduced, but these efforts were not too successful and the difficulty of handling fast-settling material in thickeners and the more sensitive operation made the development questionable. At least two plants attempted to increase the acid strength and reduce the size of the plant by direct filtration of the reaction slurry in two stages. This attempt was not very successful because of the inability to thoroughly control the gypsum precipitation and the inadequacy of the filtration equipment then available. In this industry, as in many others, the development of improved equipment and improved processes have gone hand in hand and have been mutually dependent on each other for their success.

Toward the end of this period, that is to say from 1927 to 1932, two groups were working intensively on this problem. One was a Swiss company, Kunstdünger Patent Verwertungs A.G., with a research laboratory in Berlin; the other a Swedish group, Kemiska Patenter, with headquarters in Landskrona, Sweden. The former group, known as K.P.V., was a combination of the Dorr interests and Mr. Frans Liljenroth. The latter group was headed by Mr. Sven Nordengren of the Swedish Superphosphate Company and cooperated with the German Lurgi interests.

Nordengren and his associates[29] first attempted to produce directly a very strong acid, 40 to 50 per cent P_2O_5, and this, for the reasons which will be developed in more detail later, entailed the production of anhydrous calcium sulfate[22]. They carried out the digestion under pressure and at elevated temperature, but the problem of suitable materials of construction was serious and the filtration of this strong hot acid extremely difficult. Their next step was to establish the conditions necessary, to produce a stable semi-hydrate of calcium sulfate which would not set, or hydrate, when washed[14, 23], thus making it possible to operate at atmospheric pressure and to reduce the reaction temperature to around 100°C. The most difficult problem encountered was the filtration of this slurry and, after considerable work, a special belt filter was developed[23] known as the Landskrona or Lurgi filter, which represented a great advance in the art of filtering phosphoric acid slurries. As more experience was gained with this filter and more efficient methods of evaporating phosphoric acid were developed, the conclusion was reached that the economies in producing an

especially strong phosphoric acid did not justify the attendant complications; today, the process recommended produces a 25 to 30 per cent P_2O_5 acid, depending on the grade and source of rock[23, 30]. This group has recently again taken up the production of anhydrite and 40 per cent P_2O_5 acid. The process, according to published data, is rather complicated and has not been commercially demonstrated.

The K.P.V. group worked along somewhat different lines. It also established the equilibrium conditions for the production of gypsum and semi-hydrate but concentrated on the principle of recrystallization, that is, initially producing one form of calcium sulfate and then causing it to recrystallize as gypsum. This group also produced a 40 per cent P_2O_5 acid, but proposed to produce initially the semi-hydrate of calcium sulfate, filter this off from the strong acid and then recrystallize to gypsum, refilter, and and complete the washing[18, 19]. By this method of recrystallization it was possible to produce excellent, coarse crystals, and knowing the equilibrium conditions, it was relatively easy to control the reaction. This method is especially applicable to phosphate rocks difficult to treat by conventional methods. The K.P.V. group, in a further effort to control the crystallization so as to produce a strong acid, proposed recirculating unseparated reaction products in sufficient quantity to provide the phosphoric acid necessary to dissolve the P_2O_5 as monocalcium phosphate and then to add the sulfuric acid and precipitate hemihydrate of calcium sulfate[20]. It was found, however, that the high concentrations and high temperatures necessary to produce hemihydrate introduced serious corrosion and filtration problems. The ultimate evolution of these ideas led to the production of a 32 to 33 per cent P_2O_5 acid and the direct production of a rapidly filterable gypsum[3, 38]. The process required very close control of the supersaturation conditions, but the problem was solved by the invention of the recirculation, or Dorrco Strong Acid Process[39], which will be described in more detail later.

It should be noted that, simultaneously with the development of these improved reaction and filtration steps, the equipment and processes available for phosphoric acid evaporation were also undergoing great improvement.

The Davison Chemical Company, of Baltimore, Maryland, has done a great deal of work on processes for producing granular superphosphate. As an offshoot of this work they developed a process for producing phosphoric acid which should be mentioned, although to the author's knowledge it has not gained commercial acceptance[32]. Superphosphate is produced in the usual way and then granulated. The granules are charged into a battery of leaching or percolation tanks and treated with sulfuric acid. The acid travels countercurrently through a series of such vats. The super-

phosphate is converted in place into gypsum which is washed and then flushed from the tanks. It is claimed that a 40 per cent P_2O_5 acid can be thus produced.

The Davison Chemical Corp., has also proposed a very novel method of producing a concentrated, low fluorine, phosphoric acid[21a]. Finely divided, dry phosphate rock is mixed with 98 per cent sulfuric acid, the mixture is heated to from 200 to 300°C to form a so-called clinker which is leached with water to form phosphoric acid. During the mixing and heating steps about 90 per cent of the fluorine is volatilized. It is claimed that an acid with up to 54 per cent P_2O_5 can be produced by this process. The fluorine is said to be low enough for direct use in the manufacture of phosphatic animal feed supplements.

A process following a very novel approach to this problem has been proposed by John H. Coleman,[6, 7] for producing high concentration and high purity phosphoric acid or alternatively a high analysis material for long distance shipment. Briefly, ground phosphate rock is mixed with 70 per cent phosphoric acid in proportions to give a $CaO:P_2O_5$ ratio between 5:3 and 5:4. Calcination of this material at 200°C drives off 95 to 98 per cent of the fluorine, and the resulting product is a complex polyphosphate. This can be used for the production of a concentrated phosphoric acid by digestion with a mixture of concentrated sulfuric acid and 60 per cent phosphoric acid giving a pyrophosphoric acid which rapidly hydrates to the orthophosphoric acid. The calcium sulfate is filtered off and washed, and it is claimed that a 70 per cent phosphoric acid can be produced.

THE DORRCO STRONG ACID PROCESS

This process,[39] as previously mentioned, seems to represent the most modern development of the wet process. It has been tried and proved by seventeen years operation at the plant of the Consolidated Mining and Smelting Company at Trail, B. C.[3, 38]. The recently constructed plants of Mathieson Chemical Co. (formerly Southern Acid & Sulphur Co.) at Houston, Texas, and Fisons, Ltd., at Immingham, England,[2a] seem a far cry from the usual heavy chemical plants in their convenient arrangement, concrete and steel construction, cleanliness, airiness, freedom from dust, and general efficiency of operations.

The flow sheet of the process is shown diagrammatically in Figure 3 and a general arrangement of a hypothetical plant in Figure 4. The sulfuric acid is diluted with weak phosphoric acid in mixing heads and added in two stages to the recirculated slurry in two violently agitated small mixers. The rock dust is then flash-mixed into the acidified slurry. Agitation is continued in two or three more agitators with simultaneous cooling with low-pressure air. The completely reacted slurry is held in a surge tank before filtration. Slurry from the last reaction tank is pumped or recycled to the

head of the system. The fumes are drawn off the various agitators and mixers and through an absorption or fluorine recovery system by exhaust fans. The slurry is pumped to the filters, which are either of the belt pan or disk horizontal type. The 32 to 33 per cent acid produced is already strong enough for the production of ammonium or sodium phosphates. Where used for the production of triple superphosphate or food grade calcium phosphates, it must be further concentrated by evaporation. Recoveries by this system are from 94 to 96 per cent.

Chemistry of the Process

Virtually all phosphate rocks, except those of very recent origin, have a definite fluorine:P_2O_5 ratio, corresponding fairly closely to that in fluor-
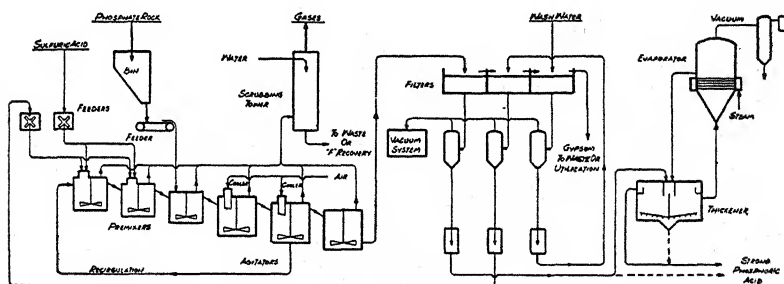
FIGURE 3. Flow sheet of the Dorrco System for manufacturing concentrated phosphoric acid by the wet process.

apatite, $3Ca_3(PO_4)_2 \cdot CaF_2$. In addition, all phosphate rocks contain many impurities. These include organic matter; iron and aluminum oxides; silica; carbonates, sulfates, and chlorides of lime and magnesium; and small quantities of sodium, potassium, titanium, zinc, copper, manganese, arsenic, chromium, vanadium and uranium.

The principal reaction occurring in a phosphoric acid plant is the reaction between tricalcium phosphate and sulfuric acid to give soluble phosphoric acid and insoluble calcium sulfate. However, there are a number of minor reactions occurring, the more important of which are shown below:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF \tag{1}$$

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O \tag{2}$$

$$Na_2O \text{ (or } K_2O) + H_2SiF_6 = Na_2SiF_6 \text{ (or } K_2SiF_6) + H_2O \tag{3}$$

$$H_2SiF_6 + Heat \text{ and/or Acid} = SiF_4 + 2HF \tag{4}$$

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2 \tag{5}$$

$$Fe_2O_3 \text{ (or } Al_2O_3) + 2H_3PO_4 = 2FePO_4 \text{ (or } AlPO_4) + 3H_2O \tag{6}$$

$$CaCO_3 + H_2SO_4 = CaSO_4 + CO_2 + H_2O \tag{7}$$
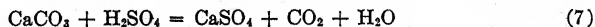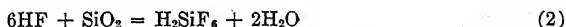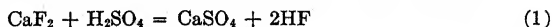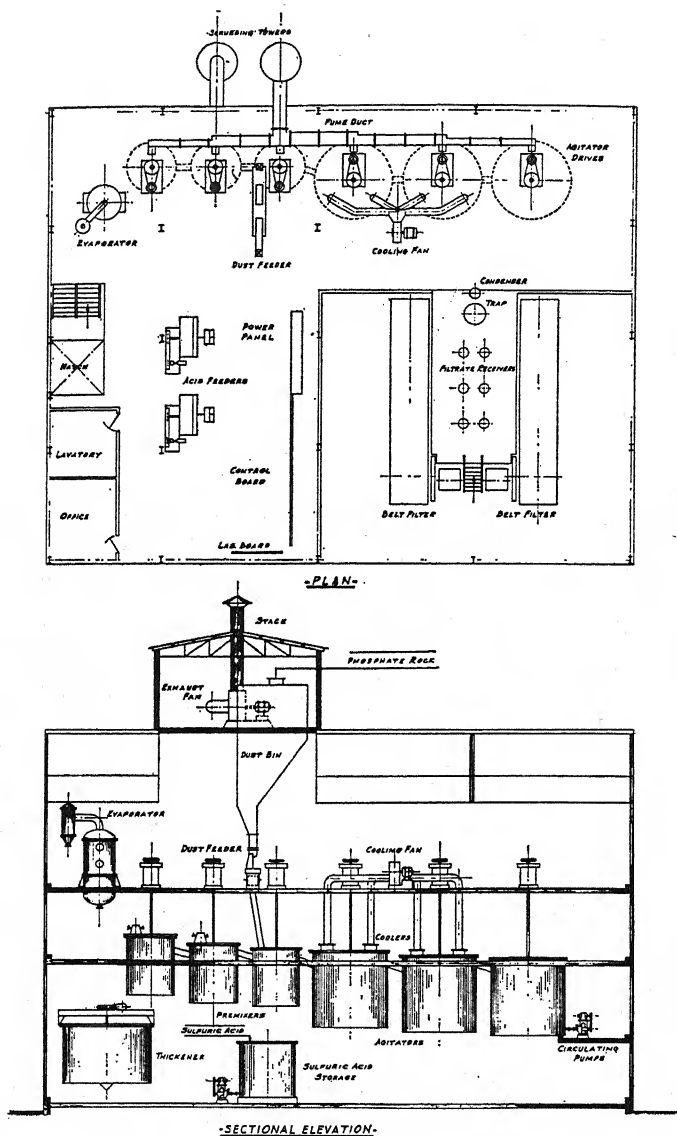
FIGURE 4. General arrangement of hypothetical plant for producing strong phosphoric acid by the Dorr Process.

The HF released, equation (1), reacts almost immediately with the silica (always present) to form fluosilicic acid (2). The silica which is attacked

in this way is apparently principally present in the form of silicates (such as clay) which are more readily available than silica in the form of sand. Any sodium or potassium reacts to form sodium or potassium fluosilicates (3). These particular compounds are a source of considerable trouble as the phosphoric acid will, in most cases, be saturated with them; and since they have steep solubility curves (vs. temperature), they are a primary cause of scale formation in pipelines and equipment. In this respect, all solutions are also saturated with calcium sulfate, which precipitates on cooling or when there is a change in the sulfate concentration. In the presence of strong sulfuric acid and at high temperatures, the hydrofluosilicic acid is decomposed and silicon tetrafluoride gas is evolved (4). This occurs wherever sulfuric acid is added or at high temperatures, and especially if any air is blown through the solutions. In the presence of moisture (in fume ducts and scrubbing towers) the tetrafluoride gas is converted into silica and hydrofluosilicic acid (5).

Practically all the iron and aluminum present in the phosphate rock is taken into solution as iron and aluminum phosphates (6). Calcium carbonate, which is one of the principal gangue materials in some deposits, is a consumer of sulfuric acid (7). Silica in excess of the fluorine is unaffected. Some African rocks are deficient in reactable silica and HF corrosion is a problem.

The principal reaction occurring is the decomposition of the tricalcium phosphate thus:

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4 \qquad (7)$$
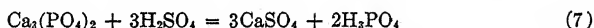
The reaction can be better understood by visualizing it in two separate steps:

$$Ca_3(PO_4)_2 + 4H_3PO_4 + \text{``X''}H_3PO_4 = 3CaH_4(PO_4)_2 + \text{``X''}H_3PO_4 \qquad (8)$$

$$3CaH_4(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 6H_3PO_4 \qquad (9)$$

In the first step, the tricalcium phosphate dissolves in a large excess of phosphoric acid to give monocalcium phosphate in solution (8). This will occur at any time that there is a deficiency of sulfuric acid, and undoubtedly occurs momentarily at the interface between the solid phase phosphate particles and the liquid phase phosphoric acid. Thereafter, the sulfate ions react with the monocalcium phosphate, precipitating calcium sulfate (9).

This is a very brief outline of the chemical reactions involved. Although the reactions are complicated by the impure nature of the raw materials, the chemistry is relatively simple. The corrosive nature of the impure phosphoric acid and its implications are another story. Pure phosphoric acid is not unduly corrosive; but, when it contains small percentages of free sulfuric acid, hydrofluosilicic acid and probably, for short periods, small

quantities of hydrofluoric acid, it becomes very active toward most construction materials. Another complicating factor is the physical chemistry involved in the production of the optimum type and size of calcium sulfate crystals and the maximum conversion of phosphate into phosphoric acid.

Calcium sulfate can be precipitated in phosphoric acid with various degrees of hydration, depending on the concentration and temperature of the solution. It may precipitate as dihydrate ($CaSO_4 \cdot 2H_2O$) or semihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$) or as an anhydrite ($CaSO_4$). The anhydrite may, in turn, occur in at least two forms: (1) the common, insoluble (or stable and nonhydratable) anhydrite, or (2) the so-called soluble anhydrite, which will, when the concentration and/or temperature are reduced, hydrate
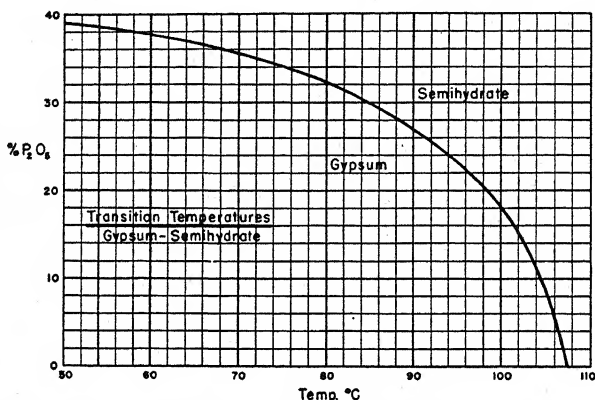
FIGURE 5. Transition temperature of calcium sulfate (hemi-hydrate) to gypsum at various concentrations of P_2O_5.

to the semi- or dihydrate form. Nordengren and his associates also found that there was a form of stable semi-hydrate which would not hydrate, or at least was sufficiently stable so that it could be washed without danger of setting during the filtration operation[23]. The curve, Figure 5, gives the transition temperatures from semi-hydrate to gypsum at various P_2O_5 concentrations. The author has found that this theoretical curve represents only average conditions and that the practical equilibrium may vary considerably from these values in well seeded commercial systems.

The key to success in a wet process phosphoric acid plant lies in the control and operation of the reaction station. If the fundamentals here are sound, the subsequent operations of filtration and evaporation should present only normal chemical engineering problems. The objectives of the reaction station are: (1) to obtain maximum extraction of P_2O_5; (2), to produce an easily filterable calcium sulfate; and (3) to produce an easily

washable calcium sulfate so that there will be a minimum loss of soluble P_2O_5 in the waste product.

EXTRACTION LOSSES

There are two types of extraction losses. The first is due to undecomposed or unattacked phosphate rock. This can be the result of insufficient grinding or insufficient detention for complete extraction. However, experience has shown that with reasonably fine grinding losses from this cause should be negligible. Losses from undecomposed rock can also occur due to coating of unattacked rock particles with gypsum. This occurs when the sulfate content of the reaction slurry is too high. Under these conditions, precipitation is so rapid that the calcium ions dissolved by the phosphoric acid do not have time to diffuse away from the rock-acid interface before being converted to calcium sulfate. The sulfate excess above which this effect becomes serious, varies with the type of rock, concentration of acid, and other conditions. It is usually around 3 to 4 per cent total H_2SO_4. When this phenomenon occurs, the phosphoric acid not only is incompletely extracted from the rock, but the excess of unutilized sulfuric acid in the solution will increase progressively and throw the whole plant out of control.

The second type of extraction loss is in the form of citrate soluble P_2O_5 in the washed gypsum. According to studies of Weber and his associates[39], this loss is due to the formation of a solid solution of dicalcium phosphate, $CaHPO_4 \cdot 2H_2O$ in the gypsum. That is, as the gypsum crystallizes out, it does not do so as pure calcium sulfate but HPO_4 ions substitute for a certain percentage of the SO_4 ions in the crystal lattice. It is in an exactly similar manner that some galena contains silver sulfide which cannot be separated from it mechanically since Ag_2S molecules replace a certain percentage of PbS molecules in the crystal lattice. This type of P_2O_5 loss arises from the fact that dicalcium phosphate crystallizes in the same crystal system as gypsum and has very nearly the same crystallographic constants. The higher the sulfate content of the solution, the less the loss; while the greater the P_2O_5 content of the solution, the greater the loss. This loss is greatest in solutions high in CaO and low in H_2SO_4. To minimize this type of loss, a slight but definite excess of SO_4 ions must be maintained throughout the reaction system.

FILTERABLE AND WASHABLE GYPSUM

The semi-hydrate of calcium sulfate can be obtained in a very rapidly filtering form. For the reasons stated elsewhere, the high concentration and temperatures necessary for its formation and other difficulties have made it uncommercial to produce this form of calcium sulfate. In the case

of gypsum it has been found that the best filtration characteristics are exhibited by rather large individual rhombic crystals of a shape wherein the length does not exceed two or three times the width and which have substantial thickness. Such crystals under the microscope will appear diamond shaped with heavy black edges indicating thickness. It is possible, and rather usual in plants with poor reaction control, to obtain crystals which are long, thin needles. These filter very rapidly, but they give a moist filter cake which occludes a great deal of acid difficult to remove. If they are exceedingly fine, they may form star-like clusters which are even more objectionable. When the crystals are too small they tend to agglommerate, and this type of gypsum, although it may filter well, washes very poorly. Under some circumstances the crystals may occur in thin plates, which give an exceedingly sloppy filter cake. This control of the reaction to give the proper type, size, and shape of crystal is important to the smooth-running and efficient operation of a phosphoric acid plant.

Assuming that the proper type of gypsum crystal is obtained, the filterability and washability appear to depend chiefly on the size of the crystals. The size is inversely proportional to the number. Therefore, as few crystals as possible are desired and, to this end, the avoidance or minimization of the formation of crystal nuclei is a major requirement. It is well known that the number of crystals formed in precipitating a quantity of a solid substance is a function of the concentration of the reacting substances in the solution phase of the reacting mixture. All crystallization or precipitation is induced through a supersaturation of the solution phase. Supersaturation will occur when either one of the two reactants, CaO or SO_4, is added to a saturated reaction system. This means it will occur if sulfuric acid is mixed with phosphoric acid saturated with CaO or when rock is introduced into the reaction slurry.

The Dorrco Strong Acid Process[39] is an attempt to control this supersaturation and to maintain throughout the reaction system the sulfate concentrations which are most favorable to the maximum extraction of P_2O_5. In this system supersaturation is kept at a minimum at all points in the reaction system: first, by maintaining a very large circulation of unseparated reaction products so that the sulfuric acid is greatly diluted and kept at a very low value throughout the system; and second, by maintaining an excess of sulfuric acid at all points in the system so that at no time is there any substantial concentration of unprecipitated CaO ions. The use of unseparated reaction products for this dilution has the added advantage that an enormous crystal surface is available, which discourages the formation of new crystal nuclei. Premixers giving relatively violent agitation are provided at the points of acid and rock introduction so as to minimize local high concentrations of either ion.

Acid Strength

As mentioned previously, while calcium sulfate can occur with different degrees of hydration, practically all present-day phosphoric acid plants are operated to precipitate the dihydrate. It is possible in a properly seeded system, at temperatures under 65°C, to produce up to 40 per cent P_2O_5 acid without forming the semi-hydrate. However, above 32 to 33 per cent P_2O_5 the crystals rapidly become smaller and exhibit a tendency to agglomerate. Maintaining reaction temperatures below 65°C greatly increases the cooling problem. It is possible to produce as high as a 38 or 39 per cent acid, but the filter displacement is poor and, with this strong viscous acid, double filtration is necessary to obtain reasonably efficient displacement of the acid in the gypsum cake. For this and other reasons, 32 per cent P_2O_5 seems to be the most economical strength when precipitating the calcium sulfate as gypsum. There is a possibility that plants in the future may again attempt to increase capacities and produce stronger acids by precipitating the calcium sulfate in the semi-hydrate or anhydrite form. New equipment, construction materials, and techniques may make this feasible.

Temperatures

The filter fabrics, if exposed to excessive temperature, are subject to rot, shrinkage, or deformation, depending on the type used. These effects are negligible at lower temperatures. Phosphoric acid solutions all contain free sulfuric and hydrofluosilicic acids and these combinations of acids are extremely corrosive to most materials, especially at elevated temperatures. High temperatures preclude the use of rubber. The solutions produced are all saturated with gypsum and, with many types of phosphate rock and under certain conditions, also with sodium and potassium fluosilicates. As a result, the solutions are scale-forming and pipelines, filter cloths, and filtrate receivers are endangered. The lower the temperatures carried throughout the plant, especially at the filters and in pumps and pipelines, the smaller will be the temperature drop and the less difficulty will be encountered from crusts and scaling. At higher temperatures the reaction will be accelerated, although there is no evidence that the ultimate extraction is any greater. Filter capacities at, say 85°C are, however, considerably increased. In general, it seems that the preponderance of arguments are in favor of low temperature operation, 65° to 75°C. Due to the exothermic nature of the reactions, when producing a strong acid and using concentrated sulfuric acid, artificial cooling is required except in small plants. Some plants use low-pressure air for cooling by evaporation. This has the added advantage that it permits the production of stronger acid or, alternatively, the use of larger quantities of wash water.

By-Products

Several by-products are being or can be recovered in the manufacture of phosphoric acid by the sulfuric acid process. Some of these have considerable potential value and the problem of their economic utilization is being given careful study. These by-products are calcium sulfate or gypsum, fluorine compounds, iron and aluminum phosphates, vanadium and uranium.

Calcium Sulfate

Gypsum from phosphoric acid plants has been used for the production of plaster and precast blocks for interior partitions[4, 8]. It is possible to produce a suitable plaster from this by-product calcium sulfate, but most of the plants which have been built have been abandoned. This was due primarily to the fact that they were on too small a scale to be economic and because of unfavorable locations and other marketing conditions.

This calcium sulfate also can and has been successfully used for the production of ammonium sulfate[21]. The economics of this application are complicated and depend on the relative cost of producing ammonium sulfate from sulfuric acid, and the availability of carbon dioxide gas and reasonably priced fuel for evaporating the 40 per cent solution of ammonium sulfate obtained. The reactions between ammonia and CO_2 to produce ammonium carbonate, and between ammonium carbonate and calcium sulfate to produce ammonium sulfate and calcium carbonate are well established and involve no unusual difficulties. Plants in Germany, France, England, Belgium, Japan, and India are producing ammonium sulfate from natural and by-product calcium sulfate on a large scale. At present there are no plants in the United States, probably because the phosphoric acid plants are located where sulfuric acid can be produced cheaply. This situation may undergo a change because of the increasing shortage and cost of sulfur. Waste calcium sulfate can also be used agriculturally and as a retarder in Portland cements.

Calcium sulfate has been used in Germany, England and France as a raw material for sulfuric acid, cement clinker being produced as a by-product. A plant at Billingham, England, with a capacity of 110,000 tons of H_2SO_4 per year has been in operation since 1929. A new plant with a capacity of 165,000 tons per year is being built near Liverpool. The plants are very expensive.

Fluosilicates

In either the thermal reduction method or the wet process for manufacturing phosphoric acid, a substantial proportion of the fluorine present in the phosphate rock is driven off in the form of noxious gases that in

most cases must be absorbed or collected to avoid contaminating the atmosphere[27].

In the wet process the evolved fluorine is in the form of silicon tetrafluoride which on contact with water or steam forms hydrofluosilicic acid and gelatinous silica. Absorption towers or venturi scrubbers are provided, in which the fluorine is absorbed by water or dilute H_2SiF_6.

The precipitated silica is settled out and the solution of hydrofluosilicic acid is either marketed direct or employed in the manufacture of such products as calcium, sodium, ammonium and magnesium fluosilicates which are used as laundry sours, in the manufacture of tile, in concrete hardeners, as ingredients of insecticides and for fluorinating water supplies. Alkali fluosilicates also are recovered in the purification of phosphoric acid by addition of soluble soda salts.

A number of superphosphate plants in this country and at least one large phosphoric acid plant recover hydrofluosilicic acid and produce substantial tonnages of fluosilicates[27].

Precipitated Phosphates

In purifying phosphoric acid produced by the wet process, contaminants such as iron and aluminum may be recovered by partial neutralization of the acid with limestone or soda ash.

The precipitates thus formed consist largely of iron and aluminum phosphates and though they represent a loss of P_2O_5 from the acid solution, they are largely citrate soluble and when dried have a distinct value for fertilizer purposes.

Vanadium

Only the phosphate deposits of the western states contain sufficient vanadium to warrant its recovery as a by-product in the manufacture of phosphoric acid by either the thermal reduction method or the sulfuric acid process. The quantity of vanadium oxide (V_2O_5) in these phosphates vary from a few tenths up to nearly one per cent. So far, the shaly phosphates in this area, which are more suitable for treatment by the thermal reduction method, appear to contain larger proportions of vanadium than the higher grades of rock. Nevertheless, the amount of this relatively rare metal in the higher grade phosphates is sufficient to warrant its recovery.

In the wet process for manufacturing phosphoric acid the vanadium is dissolved by the sulfuric acid, imparting a green color to the resulting phosphoric acid. The first method for separating this element from the acid was patented by Laist[15] who proposed to precipitate it by the addition of sodium ferrocyanide. Later it was found that vanadium could be precipitated from such acid solutions as phospho-vanadic acid by the addition of

oxidizing agents such as chlorates and persulfates[2]. Frick and Woodman[9] patented a process for purifying this precipitate consisting of heating it with a solution of soda ash and hydrated lime. The phosphorus preferentially combines with the lime precipitating calcium phosphate, whereas the vanadium dissolves as sodium vanadate. The calcium phosphate is removed by filtration and the vanadium precipitated largely as vanadium oxide by the addition of sulfuric acid. These steps are repeated until the vanadium precipitate is substantially free from phosphorus. Nelson[28] subsequently proposed the substitution of ammonia for the soda ash claiming the process to be more efficient and the recovery of ammonia for reuse a relatively simple matter.

The Atomic Energy Commission has announced in the press that certain phosphate deposits contain uranium in quantities varying from $\frac{2}{10}$ to $\frac{4}{10}$ of a pound to a ton of rock. The Commission has developed processes for recovering uranium from the phosphoric acid obtained in the wet process. Several plants are being built or are projected.

<center>EQUIPMENT</center>

Crushing

Where the phosphate rock has been beneficiated by washing or flotation, it is sufficiently fine for the grinding mills. This is true of all Florida Land Pebble, which is usually $-\frac{3}{8}$ inch. Rock obtained from vein mining operations is in coarse lumps and must receive a preliminary crushing. Any of the conventional ore-crushing equipment is suitable for this purpose. Jaw crushers and swing hammermills are most often used, with the latter usually closed-circuited with mechanical vibrating screens. For large tonnages, gyratory crushers could be considered and also rolls in closed circuit with screens.

Calcination

Phosphate rocks high in organic matter must often be calcined to eliminate excessive foaming in the phosphoric acid plant and, in many cases, blinding of filter fabrics. Also, in the case of phosphoric acid to be used in the production of pure phosphate chemicals, it is advantageous to calcine the rock to eliminate color in the finished products.

This calcination is usually carried out in rotary kilns although at least one plant is using multiple hearth furnaces of the McDougall type[16]. The size to which the rock must be reduced before calcination varies with the type of ore. In some cases $\frac{1}{4}$-inch rock can be calcined, whereas in others it is necessary to crush to 10 or even 20 mesh. Calcination temperatures vary from 500 to 900°C (900 to 1700°F). At the lower temperatures the organic matter is granulated but not actually burnt off.

The new FluoSolids system for calcination which is being exploited by the Dorr Company holds promise of being advantageously applied to this problem of calcining high organic phosphate rocks. A unit is being installed in Greece for calcining Tunisian phosphates. The organic matter supplies some of the necessary fuel and with multiple compartment units the fuel consumption should be exceedingly low. Very close temperature control can be obtained with this FluoSolids system.

Grinding

During the period 1917 to 1930, when most of the weak-acid Dorr Systems were being installed, wet grinding was very popular. The equipment used was pebble mills, lead or rubber-lined, with flint block or silex linings set in acid-proof cement[33]. The grinding media were high-grade flint pebbles, usually imported from Denmark. The rock was ground in weak phosphoric acid obtained as wash liquor from the thickeners. This wet grinding had the following advantages: it was an initial method of getting the rock into solution, the power consumption was somewhat less than with the dry-grinding equipment available at that time, and the dust loss attendant on dry-grinding was eliminated. One of the largest phosphoric acid plants in the world still uses wet grinding[3]. The 7' x 16' mills each handle about 80 tons of rock per day and the linings are good for 30,000 tons. Pebble consumption is 1.5 lbs/ton. Power consumption is approximately 20 kwh per ton of rock ground to 70 per cent—100 mesh.

Most of these earlier plants were relatively small by present day standards. A number of factors have combined to make dry grinding, under average present day conditions, considerably more attractive. The dry-grinding equipment has undergone extensive development. The available equipment today has greater capacity and is more rugged and efficient than was available when wet grinding was in its heyday. The larger plants, which are necessary because of high labor costs and high construction costs in order to obtain economic operation, would require a large number of wet-grinding units, whereas the same capacity can be obtained in one or two large, dry-grinding mills. In plants producing triple superphosphate it is necessary to dry grind the rock required for the acidulation and, rather than provide small separate equipment for the purpose, it is usually better to provide one large, central, dry-grinding plant. Wet grinding is responsible for some citrate soluble P_2O_5 loss due to the tendency, in a sulfuric acid-deficient environment, to precipitate dicalcium phosphate in solid solution in the gypsum.

Equipment for grinding phosphate rock is described in Chapter 15 covering the production of superphosphate. The equipment for phosphoric acid should be the same as that used in modern superphosphate plants. Suitable

equipment for large installations is the Raymond type of mill with the rock ground to 85 to 90%—100 mesh. Power consumption is about 18 to 20 kwh per ton. One man can operate the average grinding installation so that labor charges are inversely proportional to tonnage. The conveying and handling of phosphate rock dust has been given considerable study. The best equipment for small tonnages is probably one of the various types of bulk conveyors. For large and complex installations a pneumatic fluid solids system, such as the Fuller-Kinyon, makes a very fine arrangement.

Feeding

This is a phase of phosphoric acid plant design which has undergone study and development and is an important part of a successful operation. In the early days, batch weigh scales were used and were followed by various forms of volumetric feeders, such as belts, screws, and disk and pan feeders. Since the weight per cu ft of phosphate rock, especially when finely ground, varies considerably, volumetric feeding is not sound. Consequently, more accurate weight feeders were adopted. The earlier machines depended upon a scale beam to provide the necessary power, through a system of levers, to actuate a control gate, and were thus inherently inaccurate. Many units of this type are still in operation and with modification and careful operation give fairly satisfactory service. In recent years, these belt feeders have been improved by providing a powered feed regulation controlled by the scale beam. The type of unit now installed in the modern continuous, nearly automatic plant is a rather expensive, but highly refined and very satisfactory evolution of this principle. Special design and adaptation for phosphoric acid plant service is required. Phosphate rock dust is unusually difficult to handle. Under certain conditions it will flow like water and under others will pack and channel so badly that, unless the bin and feed equipment are very carefully designed, it is almost impossible to get consistent feed with even the best of equipment.

In the earlier plants, the sulfuric acid feeding equipment was relatively crude. Weirs, syphons, and valves were used and in some places batch weighing was resorted to. The most successful device has been a type of rotary scoop known as the Howard Acid Feeder[12]. Whereas this may seem to be a rather crude device, actually it has been developed to the point where it is exceedingly reliable and accurate and lends itself to remote control, totalization, and other instrumentation, which makes it very suitable for the modern plant. Some plants are using rotameters. The older types were not sufficiently accurate or reliable but the automatic, electrically controlled and recording type has interesting possibilities.

The weak phosphoric acid wash liquors used for diluting the reaction slurry should also be fed with some accuracy. The principal difficulty in applying the usual types of flow meters and control devices is that this

acid carries suspended solids and is both scale-forming and corrosive. The scoop type of feeder has been successfully applied.

Agitation

The reaction between phosphate rock and sulfuric acid is now carried out continuously in a series of agitators. In the early days, the Dorr airlift type of agitator was rather generally used. One plant used and continues to use Pachuca agitators. Paddle agitators also were used alone or in combination with air. With the intensive development of this process it was found that relatively violent agitation was desirable for the best results; therefore, there was a gradual trend toward the use of various types of impeller, propeller, and turbine agitators. At one plant using agitators equipped with closed impeller types of mechanisms driven by 10 h-p motors, it was found that, by increasing the intensity of agitation by doubling the power input, the throughput for the same extraction (and other results) could be practically doubled. Intensity of agitation must, of course, not be carried to the point where attrition will result in formation of fines and false crystal nuclei. The specification of agitators for this service has, therefore, become a rather specialized technique. Furthermore, it has been found that different intensities and types of agitation are required at different points in the reaction system.

The type of construction of the agitator tanks leaves a considerable choice depending on costs and other considerations. Wood and steel tanks are most commonly used. Steel gives a somewhat better support for the lining and where surplus reaction heat must be dissipated, the use of steel minimizes the amount of mechanical cooling that must be provided. Where heat must be conserved, as in the case of small plants, the insulating advantage of wood may be of some value. Wood tanks must be lead-lined and steel tanks may be either brick, lead or rubber lined. With the rapidly increasing cost of lead, some consideration has been given to the use of stainless steel tanks, especially very light steel with a reinforcing or backing of structural steel members. The temperature carried in the reaction system will affect the choice of rubber as will also the question of maintenance and repair. Lead linings must be protected against erosion as phosphoric acid slurries are extremely abrasive. While some of the earlier plants used wood protective linings, a chemical brick set in acid-resisting cement is far more satisfactory. With turbine agitators, peripheral baffles are necessary and will affect the design of the tank and lining. Provision must be made for removing the coarser material which tends to segregate in the lower part of the tank. The agitators are covered and vented.

In the Dorrco Strong Acid Process the agitators also accommodate the air-cooling distributors and the acid-mixing heads[13].

The optimum dilution to use during reaction, the temperature, and the

retention time to be provided are complicated by many factors. One or two can be mentioned. While the attack is very rapid, crystal growth is improved by slowing up the reaction. Also sufficient volume or buffering should be provided to take care of unavoidable inaccuracies in the feeding devices, variations in the analysis of the raw materials, and the time required for analysis and correction.

Fume Control

A very important feature of a well-designed phosphoric acid plant is a thoroughly adequate system of handling the fumes given off during the reaction and especially at the points of sulfuric acid addition. In many plants this has been taken care of very casually by providing hoods or ventilators over the agitators or stacks through the roof and depending on natural draft and wind to guide the fumes to one's neighbors. In the newer plants a general fume collection system is provided with connections to the agitators and other equipment requiring ventilation. The entire system is kept under a negative pressure by exhaust fans and the fumes are scrubbed with water in packed or spray towers. Provision must also be made for catching any acid spray or mist. The size and number of towers or scrubbers vary with the degree of fume removal desired, depending usually on whether fluorine is to be recovered and the character of the neighborhood where the plant is located.

Filtration

The earliest type of continuous filtration equipment was the rotary drum filter. These were usually of wood construction with lead piping and, in some cases, cast lead construction. Filter cloths were of wool or nitrated silk or cotton. These filters were used, in most cases, following several stages of decantation in Dorr Thickeners so that the corrosion and scaling conditions were not too severe. At least two plants were built, however, using two-stage filtration on drum filters directly following the agitators. The first application of the Dorrco Strong Acid Process at Trail, British Columbia, used Dorrco Internal Drum Filters in two stages (Figure 6). This plant was later altered to a three-stage operation[3]. The filters are lead-lined with rubber-lined valves and miscellaneous stainless steeel parts. The filter cloth used is "Vinyon." The original filters were rubber-lined but the lead-lined construction has been found more satisfactory. This plant has been in operation for almost 18 years, and the operators consider these filters satisfactory for their particular service[3].

With the development of the horizontal types of filters, the use of drum filters in phosphoric acid plants has gradually become obsolete. These comprise the rubber belt type (Lurgi-Landskrona), the Oliver Horizontal,

the Tray Belt Type (Giorgini) and others. Since these filters represent a very definite advance in the art and since, coupled with the production of strong acid by the recirculation system of reaction control, they represent the best modern practice in phosphoric acid manufacture, they will be described in some detail.

The belt or band filter variously referred to as the Landskrona, Nordengren, Lurgi, Stokes, or Mercer filter was, as previously mentioned, developed by Nordengren and his associates in the early 1930's[29, 35]. It com-
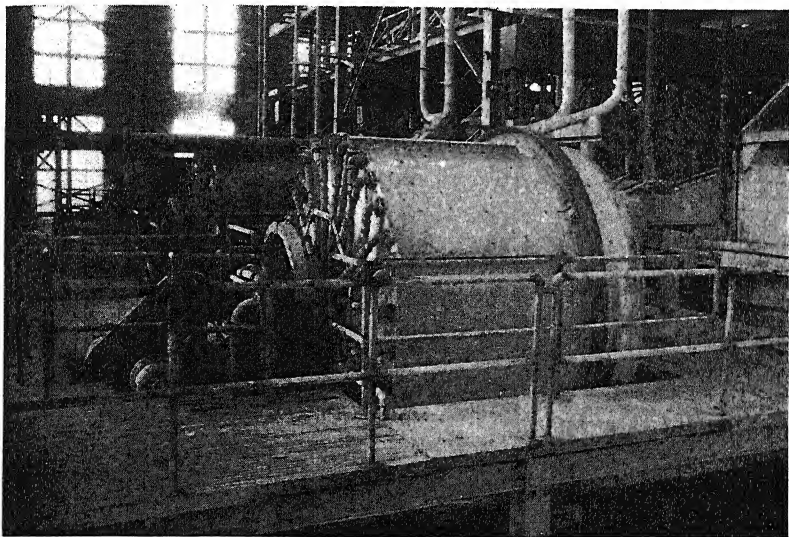
FIGURE 6. Drum vacuum filter for filtration of phosphoric acid produced by the sulfuric acid process.

prises two endless rubber belts carried on large diameter pulleys. Between the pulleys, and running longitudinally under the belts, is a narrow vacuum box flanked by ribbed decks for supporting and troughing the belts. The carrier belt is of reinforced rubber construction and is provided with raised edges for receiving the perforated belt and with centrally located, longitudinally spaced slots. These communicate with a continuous slot in the cover of the vacuum box. Supported by the carrier belt is a perforated, pure rubber belt with molded studs and transverse ribs on its lower side to provide paneled filtrate receiving spaces. The filter cloth, in the form of an endless belt, is supported by the perforated belt. The filtrate is drawn through the perforations then gravitates transversely to the slots in the carrier belt and through these into the vacuum box. Transverse flexible

dams above the belts are provided to divide the filter area into several sections. The feed is introduced onto the first section and forms a cake, which then passes under the second or cake-forming dam. In the second section, an acid wash is applied. In the third section wash water is introduced and in the final section the cake is sucked dry. Upon release of the vacuum, the cake breaks away freely from the filter cloth as it passes over the drive pulley and a water spray completes the removal. Adjustable partitions divide the vacuum box into several compartments and the various strengths of filtrate are kept separate. On the return, the filter cloth is separated from the rubber belts and thoroughly rinsed by water sprays. The filter sections are kept flooded, which aids in forming a uniform cake, results in very effective downward displacement washing, and minimizes vacuum requirements. A variable speed drive gives belt speeds of from 7 to 14 feet per min. These filters are built in the following sizes:

U. S. designation	#5	#10	#30	#40	#50
European designation	—	—	3 meter	4 meter	5 meter
Net filter area (sq ft)	5	10	32	63	54

Belts have been made of neoprene but a high grade natural rubber is preferable. Vacuum box, dams, deck, and feed and wash boxes are of 316 stainless steel. Pulleys are rubber covered. Filter cloths are of wool or synthetic fiber.

The above covers the design, where troughed belts are employed. The newest design of this filter reverts to the original idea of a flat belt with upstanding molded edges. This has several advantages, such as uniform cake thickness, ease of dam construction, and better tracking of the filter cloth. The biggest improvement is the provision of a square, rubber drive belt or band between the vacuum box cover and the carrier belt[24, 36]. This is driven by twin chains carrying cross pins piercing the belt. This takes the strain off the large, expensive carrier belt, the life of which, it is claimed, is thereby greatly increased. The replacement of the drive belt is simple and inexpensive.

The life of the carrier belts is from 2 to 5 years and of the perforated belts, 1 to 2 years. Very few other important parts are subject to serious wear, corrosion, or replacement.

Operating data were obtained from a plant (see Figure 7) using recirculation and producing 30 to 32 per cent P_2O_5 acid. Capacity, maximum, 3 tons of rock per square foot per day, average 1.5 to 2 tons. Cake moisture, 25 to 30 per cent. Washing loss, 1 to 2 per cent. Filter cloth life, 1,000 hours. Feed, 65°C. Wash liquor returned to the reaction, 25 per cent P_2O_5. Recirculated wash filtrate, 5 per cent P_2O_5.

Thirteen of these filters have been installed in phosphoric acid plants in the United States. There are a number of small installations abroad and a large new triple superphosphate plant in England put five, 5 meter units, into operation in 1951.

The Oliver Horizontal Rotary Filter, developed in 1945, is a vacuum filter with the filtering surface revolving in a horizontal plane or on a vertical axis (see Figure 7). Gravity aids the flow of filtrate, which is downward at all times. By means of properly spaced weirs or spray pipes, various strengths of wash liquors can be applied and, by the use of a multiple-port
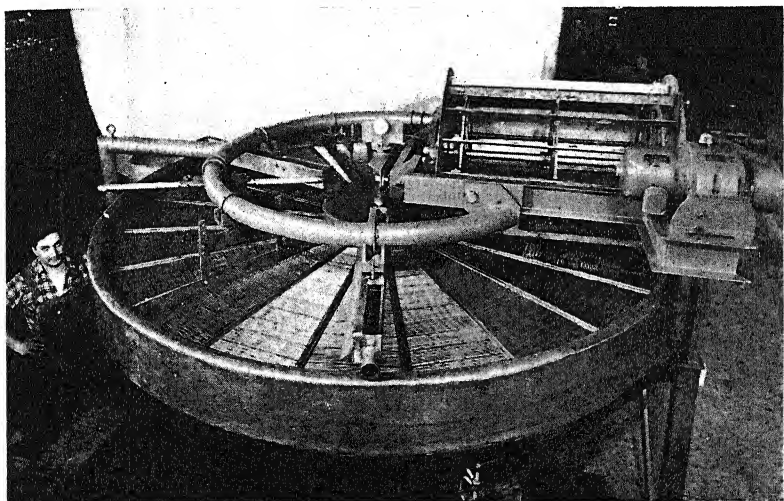
FIGURE 7. Oliver horizontal rotary filter used in the filtration of relatively strong phosphoric acid produced by the wet process.

valve, various strengths of liquors can be drawn off separately for use in countercurrent washing. The main part of the filter is a circular shallow pan, supported on a ball-bearing turntable and revolved at from $\frac{1}{3}$ to 1 rpm by a sprocket meshing with a roller chain mounted on the pan trunnion. The pan is divided by grooved radial division strips into twenty pie-shaped sections with sloping bottoms and with a port at the bottom of the apex of each section communicating with the valve. Renewable drainage grids support the filter cloth which is caulked into the grooves around the periphery of each section.

A flexible dam is provided near the feed channel for confining the feed pulp. Similar dams, if necessary, are provided to confine the wash liquors. An air blowback is applied to the cloth at the point of feed in order to mix

the residual cake with the new feed. Adjustable weirs or wash pipes are provided for distributing the feed and wash solutions. These are carried on a frame which can be swung out of the way when work is to be done on the filter. Two methods of removing the cake are available:

(1) If the cake is to be repulped and pumped to another stage or to waste, a radial scraper blade attached to a ramp removes the cake down to within about $\frac{1}{8}$ inch of the filter cloth. The cake is pushed up the ramp by a paddle wheel into a radial trough from which the cake is flushed by water or repulping solution.

(2) If the cake is to be discharged without repulping, a discharge scroll with a shroud is provided. The scroll removes the cake down to within about $\frac{1}{8}$ inch of the filter cloth and discharges it over the outer rim of the filter pan into a hopper.

These filters are built in the following sizes:

Dia. of pan (ft)	3	4	6	10	11.5	13	15
Gross filter area (sq ft)	3	10	25	65	90	120	165
Weight (lbs)	6,000	6,500	11,500	23,000	26,000	30,000	35,000

The pan is of steel, homogeneously lead-lined with extruded antimonial lead drainage grids, supporting ribs and caulking grooves. The filter valve, paddle wheel, scroll, wash troughs, weirs, and pipes are of 316 stainless steel. Cloth is a monofilament synthetic plastic. Drive consists of a constant speed motor with vari-pulley drive to a vertical shaft reducer. The 3 and 4 foot units are built in stainless steel only and the larger units can be obtained in all stainless construction, instead of lead, if desired.

Operating date were obtained from a plant not using the recirculation system of reacton control and producing a 22 to 25 per cent P_2O_5 acid. Capacity, 1.4 to 2.0 tons of rock per sq ft of filter area. Moisture of the cake, 25 to 30 per cent. Wash water used, 1 part to 1 part of rock. Washing loss, 1 per cent. Filter cloth life, 60 days. Feed temperature, 85°C. Wash liquors returned to the reaction, 17.5 per cent P_2O_5. Recirculated wash filtrate, 6 per cent P_2O_5.

At least five installations of these filters, involving about twenty units, have been made in the last five years. The filter is well designed and manufactured and has many features that make it especially attractive for phosphoric acid work.

The latest type of horizontal filter to be developed for phosphoric acid service is the Tray Belt Filter developed by M. Giorgini, Manager of Dorr-Oliver Soc. a R. L. of Milan, Italy. It comprises a series of rectangular, shallow pans arranged in the form of a continuous belt. The pans overlap, and are supported at their ends on rollers riding on elliptical tracks and are

driven by chains passing over head and tail sprockets. The bottoms of the pans are ribbed to support a perforated plate or screen and the filter cloth is clamped between upper and lower portions of the pans. Running longitudinally is a narrow vacuum box with slotted cover and between the vacuum box and the pans is a rubber belt. The bottom of the pans is slotted and the rubber belt is provided with a series of holes to drain off the filtrate and apply vacuum to the pans. Operation and accessories are similar to the belt or band filter. The cake is blown out of the pans or washed out when they are in the reverse position at the drive end of the filter. The pans are washed during the return travel to continuously remove scale and incrustations.

These filters have been built in sizes from 5 to 12 square meters (54 to 130 sq ft). Five units have been installed in plants in Italy, Greece and Switzerland. Advantages of this design over the rubber belt type are elimination of the expensive drive belt, more positive drive, no difficulty with filter cloth tracking and positive separation of washes without dams and wipers. A disadvantage is the larger number of moving parts.

These horizontal filters represent a great advance over the older drum types, such as the Oliver and Dorrco. They permit the use of countercurrent washing on a single filter, thereby obviating the necessity of stage filtration, which, at best, involves complicated piping and accessory equipment. The washing is more effective since the solids settle onto the filter surface and the filter cake can be kept flooded with wash solution, thereby avoiding cracking and uneven distribution as is almost unavoidable with sprays. The filter surface is readily accessible for maintenance, observation, and control of the operation.

The belt filters have the added advantage that the filter cloth is continually exposed and accessible for washing and thorough rinsing with water on the return cycle. The Oliver Horizontal must, from time to time, be taken out of service for scrubbing and washing the filter cloth. This detail is important when filtering the scaling and crystallizing solutions obtained with some phosphate rocks, especially when producing strong acid. With the belt filter, the number of parts which must be built in acid-resisting construction are at a minimum and they can easily be made of rubber or stainless steel. On the Oliver and the Tray Belt Filter the filter cloth sections can be replaced individually.

A disadvantage of the Landskrona belt filter and an important advantage of the Oliver Horizontal and the Giorgini Tray Belt is the fact that the latter can be built in very much larger unit sizes. For structural reasons the rubber belt type is limited to a maximum size of approximately 54 square feet. This means that, in the case of large plants, a multiplicity of belt units is required, which can make the equipment cost appreciably higher as well

as increase the space requirements. In the case of smaller plants any difference is not material. With either type of filter, except in the case of very small plants, a spare unit is always advisable.

The belt filters are not suitable for stage filtration. If washing is not completed in the first stage, the cloth will be soaked with phosphoric acid, which will cool, and scale or harden, when exposed to the air on the return cycle and, if the cloth were washed, the P_2O_5 loss would be prohibitive.

Several attempts have been made to develop improved forms of the horizontal filter principle. One company in Belgium has developed a horizontal disk filter, divided into a number of pie-shaped sections, which can be individually tilted to discharge the cake. A similar filter is available in the United States but has not been used on phosphoric acid. As compared with the Oliver and Giorgini this construction seems to involve unnecessary mechanical complications.

Evaporation

In the earlier plants, evaporation was by steam coils in lead-lined tanks. The acid was also passed down through towers into which hot gases were forced. Today a number of satisfactory evaporators are available.

Nordengren has developed a hot air evaporator which is especially suitable where by-product hot air is available, as, for instance, the cooling air from the rabble arms of hearth roasters[23]. It consists of a long trough with a distributor down the middle provided with nozzles for blowing the hot air into the acid. The apparatus is open and easy of access. The main problems have been rapid scaling and corrosion of the nozzles. It is not extensively used.

Another type of evaporator which uses hot combustion gases is the Chemical Construction Company Drum Concentrator or more recently developed, Chemico High Temperature Acid Concentrator. This is an adaptation of a unit which was developed by this company for concentrating waste sulfuric acid. The gases are produced in a separate combustion chamber using oil as a fuel. They are then forced through the acid and finally scrubbed in a Pease-Anthony Venturi Scrubber for removal of any acid mist. This evaporator is expensive, but it is efficient and can handle dirty acid containing considerable quantities of suspended solids. Three plants have been equipped with this type of evaporator in the United States and one plant in Europe uses a similar unit.

The Kestner long tube evaporator has been used in France successfully. This is a steam-heated evaporator using long vertical lead tubes, which are arranged so that they can be renewed and cleaned easily.

The most successful evaporator and the one of which there are the most installations, is the Swenson. This is a single effect vacuum evaporator

using low-pressure (10 ﹟) steam. The bodies are cast lead and rubber-covered steel. In the older designs the tubes were horizontal, were initially made of lead-covered copper or stainless steel but Karbate is now preferred. The newest type uses an outside heat body with vertical tubes and thermo-syphon circulation. Vacuum is produced by a two-stage steam ejector. Tube sheet are stainless steel or lead covered. The evaporator should be provided with a vapor trap to remove acid spray and a barometric con-denser. Vapor piping is rubber-lined steel. The most serious problem in the evaporation of phosphoric acid is the tendency of the dissolved impurities, principally calcium sulfate and sodium and potassium fluosolicates, to precipitate on the inside of the body and especially on the tubes. For many years this made the use of indirect heat or vacuum evaporators relatively unattractive. The use of the Weber Recirculation System (40) has mini-mized or almost eliminated most of the trouble from this source. This process, in brief, consists of concentrating to a slightly higher concentration than is desired and mixing this concentrated acid with dilute feed acid. This results in a precipitation of impurities since the soluble impurities are less soluble in concentrated acid. The precipitated solids are removed in a small thickener and the clarified acid is recycled to the evaporators. The circulation rate is so controlled that the acid is only concentrated through a small range at each pass. With this degree of concentration, the acid supersaturates but does not precipitate spontaneously and, therefore, deposition on the tubes is largely avoided. The small amount of scale which forms can be dissolved by boiling out every week or ten days with water or soda solution. The excellent circulation obtained in the evaporator also makes the ebullition smoother and there is less scaling of the vapor lines with silica and fluosilicates; it also improves the heat transfer and capacity of the evaporator. This method of operation was first tried at Trail, B. C.

Recently one large plant installed submerged combustion units using natural gas. The fuel consumption efficiency is excellent. It requires about 1,300 Btu to evaporate one pound of water. The units are simple, although they require a considerable amount of control equipment. The principal problems have been with corrosion of the burner, the design of the burner supports, and the production of a white fume in the exhaust gases which cannot be removed by inexpensive methods. This submerged combustion has such obvious advantages where high Btu natural gas is available that these difficulties will undoubtedly be overcome.

Materials of Construction

The experiences, mostly negative, with materials suitable for resisting the corrosive attack of wet process phosphoric acid have been quite a saga. The choice, even today, is very limited, and there are several fairly com-

plete discussions in the literature[1, 41]. The suitable materials are limited to certain stainless steels, rubber, lead (when properly protected), carbon or karbate, and acid-resisting bricks or cements. Wood can be used for weak acids and under certain conditions. Piping is usually of lead, lead-lined steel, rubber or rubber-lined steel. Except for the question of price, stainless steel might also be considered. Valves are of rubber, lead, or stainless steel. It is the author's experience that laboratory tests and experiences with pure or electric furnace acid are absolutely worthless as criteria in selecting materials suitable for a wet process plant.

PLANT ARRANGEMENT AND DESIGN

A modern phosphoric acid plant is a far cry from the dirty, wet and dripping, dingy, typical heavy chemical plant of not so many years ago.

Foremost is the question of ventilation. The liquors are hot and give off noxious gases which are dangerous to workmen in certain concentrations and objectionable even when greatly diluted. The solutions are hot and steamy and, in certain localities and at certain times of the year, condensation in and on the building can be very messy. Good practice therefore, dictates closed equipment and covered tanks and launders, etc., throughout. Whereas such an arrangement makes observation of the operations more difficult, this can be taken care of by proper provision of manholes, removable sections of covers, sampling openings, and liberal instrumentation. The ideal arrangement is to maintain all the equipment under a slightly negative pressure by means of a central fume collecting and disposal system. In addition, the building should be well ventilated and plenty of openings provided in the floors, etc., so that when equipment is opened up for observation or maintenance, the fumes can readily escape and not reach dangerous concentrations.

The next consideration is cleanliness. To start with, all sources of dust should be eliminated. This means special care in handling the finely ground phosphate rock and covering and ventilating all conveyors, feeders, bins, etc. Concrete floors are the most satisfactory and, in a well designed plant, spills and acid drips should be so infrequent that acid-proofing the floor is unnecessary and unjustified. Where acid drip is unavoidable, as around the glands of certain types of pumps, and where samples are taken, etc., drip pans can be provided. As in all wet process plants, curbed and drained concrete floors should be provided wherever a spill is a possibility. Frequent hose outlets should be provided as it is desirable to wash the equipment and floors frequently. Where floors are not subject to spill they may be of subway grating. Wood floors or checker steel plate are not advisable because of difficulty in keeping them clean.

A plant can be made very much more attractive and the operators given an incentive for maintaining cleanliness by a judicious system of painting

and color combinations. For surfaces which cannot be readily or frequently cleaned, such as building steel, tanks, bins, etc., a color should be chosen which is as near to the color of the prevailing dust (probably the ground rock) as possible. Machinery which it is feasible and desirable to have the operators clean frequently should be painted some pleasing color, and motors, electrical conduits, guards, valve handles, controls, etc., should be painted fairly bright colors. A system of colors or color banding for pipelines should be established and rigidly adhered to. This is of considerable convenience to operation and maintenance and adds to the general effect of a well chosen color system.

The primary object of the entire plant arrangement should, of course, be maximum ease and accessibility for operation and especially operating control. The several stations should preferably radiate from a central hub or control point. It is possible in a wet process phosphoric acid plant to arrange the equipment so that practically all operation is from one upper floor and all of the controls, including feeders, instrument board, electrical starters, etc., can be brought together at one place. All pumps should be gathered together on one floor. A small foreman's office should be provided accessible to the control center. It is usual to provide a small laboratory in the phosphoric acid building for routine and control analyses.

Buildings are usually steel or concrete frame with concrete main and intermediate floors and R.P.M., transite, or brick exteriors with built up laminated wood or corrugated transite or R.P.M. roofing. Wood construction is not very satisfactory for a phosphoric acid plant.

Considerable instrumentation is desirable and is conducive to more efficient operation and reduction in labor requirements. Instruments should all be grouped on a central control board. The selection of instruments is not simple because of the special nature of the solutions encountered, especially the corrosion and scaling propensities of the solutions and slurries.

In at least two plants, an elaborate system for electrically interlocking the feeders and pumps has been worked out which makes the operation relatively foolproof.

There are probably few chemical plants where negative experiences are more valuable to the designer than is the case in the choice and arrangement of equipment in a wet process phosphoric acid plant. The engineering of this type of plant has undergone enormous development and it is an extremely specialized technique or art. Careful design will obviate many difficulties in operation.

Costs

The basic determining factor in the cost of phosphoric acid by the wet process is the value of the two raw materials, phosphate rock and sulfuric acid or sulfur. In certain large operations, these account for 60 to 75 per

cent of the total production cost including fixed charges. Therefore, plant
location is extremely important. Except in the case of very small plants
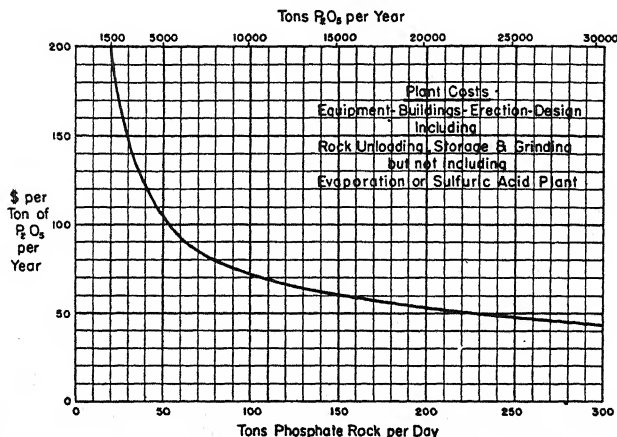
FIGURE 8. Curve showing effect of plant capacity on the capital charge of producing a ton of P_2O_5 in the form of strong phosphoric acid.
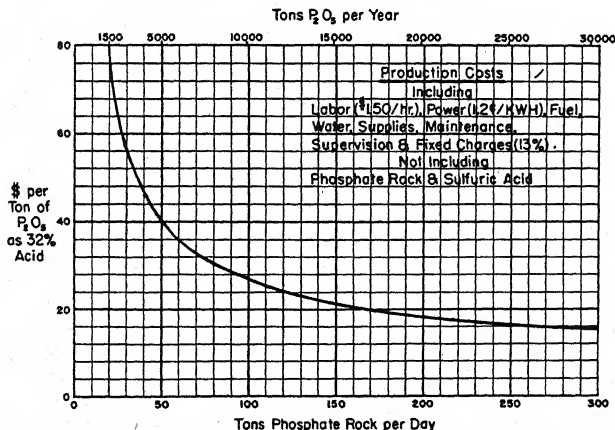
FIGURE 9. Curve showing effect of plant capacity on the cost of operation per ton of P_2O_5.

or unusual conditions as to markets it is advisable to build a sulfuric acid
unit as part of the phosphoric acid operation. The steam required for
evaporation can be obtained from the waste heat boilers in a contact sulfuric acid unit. Purchased acid is expensive and freight rates on sulfuric
acid are high. It is, of course, often possible and highly desirable to base a

phosphoric acid operation on low-cost sulfuric acid obtained as a by-product of smelter operations. In this case, it may be desirable to haul the rock to or near the source of acid.

Because the raw material cost is such a large item, extraction and recovery efficiencies are important. Modern process developments have reduced the chemical loss to an exceedingly small figure. Efficient design and a well-organized operation are even more important in reducing hidden and unknown losses and those that can result from lost time and reduced tonnage operations. A wet process phosphoric acid plant should be operated 24 hours per day and 7 days per week. A production corresponding to

TABLE 1. PRODUCTION COSTS—32% P_2O_5 PHOSPHORIC ACID

Includes: Cost of unloading and grinding phosphate rock.
Does not include: Cost of phosphate rock or sulfuric acid.
Annual expenditures: Hundreds of U. S. Dollars.

	PLANT SIZE—TONS OF ROCK PER DAY					
	20	40	60	100	200	300
Labor (at $1.50/hr) and supervision......................	574	718	861	1005	1148	1293
Power (at $0.012/kwh)........	49	103	149	280	440	600
Steam, water and supplies....	21	45	75	130	253	377
Maintenance—6% of plant cost......................	186	270	336	438	630	780
Indirect costs and depreciation —13%.....................	403	585	728	949	1365	1690
Total annual costs........	1233	1721	2149	2802	3836	4740
Annual production—tons of P_2O_5.....................	1560	3750	6030	10135	20265	30400
Production cost per ton of P_2O_5	$79.00	$45.90	$35.60	$27.70	$19.00	$15.60

capacity operation for from 330 to 350 days per year can be achieved in a well-designed and operated plant.

The extraction of P_2O_5 from the rock should average 97 to 97.5 per cent and losses of dissolved P_2O_5 in the gypsum can be kept under 1 to 2 per cent. There is always, and apparently unavoidably, a discrepancy between the accountable losses in the gypsum and the inventory recovery, which may run into unbelievable figures, especially during the initial operation; but with stable, intelligent operation it can be kept below one per cent and should not exceed 0.5 per cent. The over-all recovery, therefore, from rock to 32 per cent acid should run from 94 to 96 per cent. One very large plant recently reported 95.4 per cent recovery and 32.7 per cent P_2O_5 produced acid averages for an entire year. Losses during evaporation can be kept under 0.5 per cent.

With the trend toward very high labor costs, this item has become significant in spite of the fact that the well-arranged phosphoric acid plant is a continuous and well-nigh automatic operation and can be run with very few operators. A complicating feature is the corrosive, scaling, and

TABLE 2. OPERATING PHOSPHORIC ACID PLANTS IN AMERICA

COMPANY	LOCATION	PROCESS
Oldbury Electro-Chemical Co.	Niagara Falls, N. Y.	Electric
Anaconda Copper Mining Co.	Anaconda, Mont.	Wet
Virginia-Carolina Chemical Co.	Charleston, S. C.	Wet
Virginia-Carolina Chemical Co.	Nichols, Fla.	Electric
International Mineral & Chemical Corp.	Wales, Tenn.	Wet
International Mineral & Chemical Corp.	Mulberry, Fla.	Wet
Blockson Chemical Co.	Joliet, Ill.	Wet
Tennessee Copper—U.S. Phosphoric Products Corp.	Tampa, Fla.	Wet
Dupont-Grasselli Chemical Division	Grasselli, N. J.	Wet
Dupont-Grasselli Chemical Division	E. Chicago, Ind.	Wet
General Chemical Co.	Marcus Hook, Pa.	Wet
Tennessee Valley Authority	Wilson Dam, Ala.	Electric
Monsanto Chemical Co.	Columbia, Tenn.	Electric
Monsanto Chemical Co.	Soda Springs, Idaho	Electric*
Cons. Mining & Smelting Co. of Canada	Trail, B. C., Canada	Wet
Victor Chemical Works	Mt. Pleasant, Tenn.	Electric
Victor Chemical Works	Silver Bow, Mont.	Electric
American Agricultural Chemical	South Amboy, N. J.	Electric
Mathieson Chemical Co. (formerly Southern Acid & Sulphur Co.)	Houston, Texas	Wet
Victor Chemical Works	Tarpon Springs, Fla.	Electric
Armour Fertilizer Works	Florida	Wet
Armour Fertilizer Works	Columbia, Tenn.	Wet
Swift and Company	Florida	Wet
Westvaco Chemical Division of Food Machinery & Chemical Corp.	Pocatello, Idaho	Electric
Gulf Chemical Co.	Houston, Tex.	Wet
Texas City Chemical Co.	Houston, Tex.	Wet
Gates Brothers	Wendell, Idaho	Wet

* Not yet in operation.

abrasive characteristics of the solutions, which necessitate frequent and messy descaling and cleaning operations. Careful design can and has greatly reduced this onerous work, but it may always be a necessary evil of wet acid production. Present labor costs are such that one of the primary objects of phosphoric acid plant design must be to keep operation costs and costs for repair work to a minimum.

The other important cost factors are maintenance and depreciation,

which have assumed even greater significance with the astronomical rise in construction costs of the last few years.

Labor, maintenance, and depreciation charges are all heavily influenced by the size of plant. This can be readily seen from a study of Table 1 and

TABLE 3. PHOSPHORIC ACID PLANTS IN EUROPE AND ASIA

(Not complete)

COMPANY	LOCATION	PROCESS
I. G. Farbenindustrie	Ludwigshafen, Germany	Wet
I. G. Farbenindustrie	Piesteritz, Germany	Electric
Chemische Fabrik Budenheim	Mainz, Germany	Wet
Chemische Werk Albert	Amoneburg, Germany	Wet
Imperial Chemical Industries	Billingham, England	Wet
Albright and Wilson	Birmingham, England	Electric
Fisons, Ltd.	Immingham, England	Wet
West Norfolk Farmers Union	East Lynn, England	Wet
Establissement Kuhlman	Rieme, Belgium	Wet
Produits Chimiques de Tessenderlou	Quaedmechelen, Belgium	Wet
Metallurgique de Prayon	Engis, Belgium	Wet
Union Chimique Belge	Burght, Belgium	Wet
S. A. de Pont-Brule	Pont-Brule, Belgium	Wet
Nederlandsche Kunstmeestfabriek	Vlaardingen, Holland	Wet
Albatros Superfosfaatfabriek N. V.	Pernis, Holland	Wet
Sas V. Gent	Rotterdam, Holland	Wet
Establissement Kuhlman	La Madeleine, France	Wet
Societe St. Gobain	Rouen, France	Wet
Forenade Superfosfatfabriker	Landskrona, Sweden	Wet
Reymersholm Gamla Industrie	Reymersholm, Sweden	Wet
Silesia Verein Chemicher Fabriken	Saarau, Silesia, Poland	Wet
Montecatini	Cotrone, Italy	Wet
Montecatini	Milan, Italy	Wet
Societe Hellenique de Products et Engrais Chimiques	Athens, Greece	Wet
Uniao Fabril	Lisbon, Portugal	Wet
Nippon Chisso K. K.	Kanko, Korea	Wet
Sumitomo Fertilizer	Niihama, Shikoku, Japan	Wet
Applicazione Processi Elettrochimici	Vado Ligure, Italy	Wet

Figure 9. The economies in large-scale operation are obvious. A capacity under 60 or 70 tons of rock per day is not economical except under very special circumstances. This is also apparent in the investment required, Figure 8. Actually, when the necessity of earning a return on the investment in accessory facilities, including the sulfuric acid plant, are also taken into account, it is rarely wise to consider a plant size below 150 tons of rock per day. The most economical capacity seems to be around 300 to 350 tons. For larger capacities it becomes necessary to unitize so

much of the equipment that further economies in first cost and operation are small. It is apparent from Figures 8 and 9 that the curves are becoming very flat.

Waggaman and Bell[34] have discussed the factors affecting plant location and the relative economics of the wet process versus the thermic processes for producing phosphoric acid. Only where power is unusually cheap and sulfur expensive will the electric furnace process produce cheaper acid for fertilizer purposes. Where sulfuric acid is available from a smelting operation the wet process should invariably be cheaper.

Tables 2 and 3 list some of the wet and electric furnace installations in this country and abroad.

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13. Comparison of Sulfuric Acid and Thermal Reduction Processes for Manufacturing Phosphoric Acid

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The wet process and the two modifications of the thermal decomposition method for producing phosphoric acid not only vary with respect to the character of the raw materials and sources of energy required, but the types of equipment used and operating details are entirely different. Therefore, in comparing the economies of these methods five basic factors are involved:

(1) Cost of mining and preparing the phosphate rock for subsequent treatment.

(2) Cost of assembling the raw materials and reagents (energy) required at the most convenient points for the manufacture of finished products.

(3) Capital cost of processing plants of equivalent capacity.

(4) Detailed cost of the various manufacturing steps.

(5) Cost of distributing the finished products to established consuming centers.

Inasmuch as phosphoric acid (from which nearly all commercial phosphates are derived) is produced by these three methods, it would appear that the choice depends largely on the relative costs of manufacturing this acid by these processes. In the thermal reduction methods, however, phosphorus is obtained as an intermediate product and this element has a concentration (in terms of P_2O_5) three times greater than strong phosphoric acid.

Therefore the cost of shipping elemental phosphorus per unit of saleable product is less than that of any other phosphorus-bearing material with the exception of potassium metaphosphate. The possible economic advantage of transporting elemental phosphorus to consuming centers where it can be converted into phosphoric acid and its derivatives must be taken into consideration. A detailed discussion of the relative advantage of shipping elemental phosphorus and various phosphate products to consuming centers is given by Bell and Waggaman[1].

The relative proportions of phosphorus contained in the various products derived from phosphate rock when loaded into freight cars are shown in Figure 1.

The cost figures in this chapter have been assembled from various sources. Whereas, they apply specifically to conditions that are attainable in the phosphate regions of the western states where potential sources of electric power, fuel and sulfuric acid exist for processing the phosphate
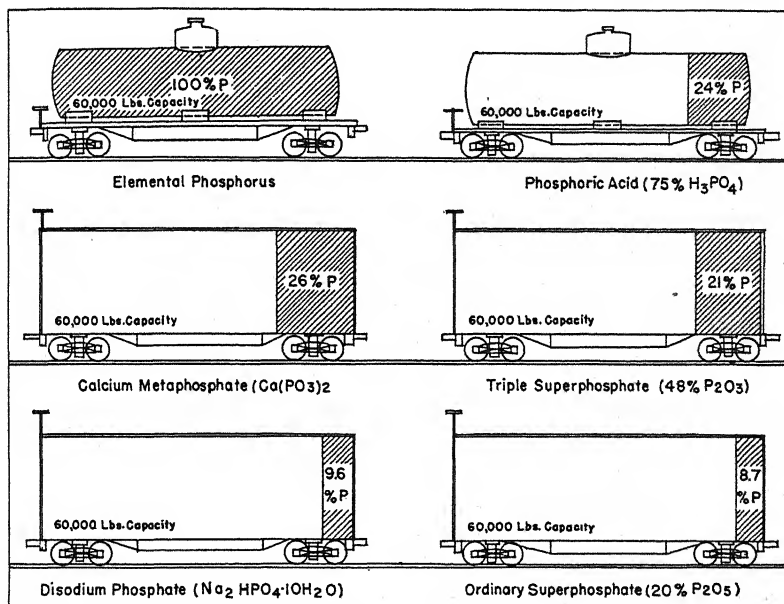
FIGURE 1. Relative proportions of phosphorus contained in freight cars loaded to capacity with elemental phosphorus and several of its important derivatives.

rock, nevertheless by use of the tabulated figures and charts which follow, anyone interested in the establishment of a phosphoric acid plant should be able to determine what process is best suited to the conditions prevailing at the time and place such an enterprise is contemplated.

COST OF PREPARATION OF PHOSPHATE ROCK FOR SUBSEQUENT TREATMENT

Although the potential reserves of phosphate rock suitable for treatment by either the sulfuric acid or thermal reduction method are ample to support an immense phosphate industry for many years, certain off-grade or marginal deposits will require beneficiation in order to utilize these deposits to the best possible advantage.

Concentration by washing and screening, as well as through the medium of classifiers and flotation, has been highly successful in the Florida phosphate fields[5, 6, 7, 8, 10, 11] and has been used to a less extent in Tennessee[4, 5, 12], but many of the lower grade phosphate strata in the western states consist of close-grained shaley and calcareous phosphates that do not lend themselves readily to concentration by either gravity or flotation processes.

Beneficiation of western phosphates has been studied by Newton and Finkelnberg[9], of the University of Idaho, and investigations are being conducted at the Salt Lake City, Utah, and the Albany, Oregon, laboratories of the Bureau of Mines, based on standard and modified ore-dressing methods.

Beneficiation

The main objective in beneficiating phosphate rock is to reduce the percentage of impurities, which either act as diluents or actually consume substantial proportions of the reagents or energy required in converting the rock into finished products.

Where phosphoric acid is manufactured by the sulfuric acid or wet method, the presence of substantial amounts of silica in the phosphate rock does not necessitate the use of a greater proportion of acid, but it does entail the handling of larger quantities of raw material and the consumption of additional time, power, and labor in pumping, filtering, and washing the insoluble residues. Moreover, the concentrated superphosphate obtained by treating highly siliceous phosphates with phosphoric acid contains considerably less phosphorus pentoxide than that manufactured by the acidulation of high-grade rock, resulting in higher transportation costs per unit of plant food in the final product.

The use of high calcareous phosphates in the manufacture of phosphoric acid and triple superphosphate by the wet method is even more objectionable. Fully as much sulfuric acid is consumed in converting calcium carbonate into sulfate as is required to convert an equal weight of calcium phosphate into phosphoric acid. Therefore, the quantity of sulfuric acid normally used must be substantially increased to take care of this impurity.

In the thermal reduction method, in which the lime combined with phosphoric acid must be converted into calcium silicate and fluxed off as molten slag, a substantial quantity of silica is essential. This means that if high-grade phosphate rock is used silica must be added to obtain a blend suitable for furnace treatment. The ratio of silica to lime ($SiO_2:CaO$) in such a charge should not be less than 1:1 and may be higher.

Since any bases in excess of those combined with the phosphoric acid

must also be converted into slag, the presence of calcium and magnesium carbonates entails the addition of further quantities of silica, thus diluting the furnace charge and increasing the amount of power or fuel required per unit of phosphorus or phosphoric acid produced.

Obviously, therefore, in beneficiating highly calcareous phosphate rock for treatment by either the sulfuric acid or thermal method, little is gained in so far as consumption of reagents or power is concerned unless the percentage of carbonates of lime and magnesia is reduced materially.

Until methods of beneficiating the marginal types of phosphate rock are more fully worked out, phosphate strata adaptable to treatment by these two methods without the necessity of upgrading are being employed, and such deposits are the only ones considered here.

Rock for Wet Process

The five steps involved in preparing phosphate rock for treatment by the sulfuric acid method are mining, handling and storing, crushing, calcining, and grinding. The rock used in this process should be relatively high grade, seldom containing less than 32 per cent P_2O_5 and preferably more. This means a selection of strata that represents a small proportion of the phosphate formation. Although mining costs vary considerably, depending on the depth of the deposit, the type of adjacent strata, and whether underground or strip mining is practicable[2, 3, 8], the over-all cost of underground mining high-grade rock under reasonably favorable conditions is estimated at \$4.50 per ton. In the case of strip mining this figure might readily be as low as \$2.00 per ton.

The second step (handling and storing) is a significant item of cost in surface or strip mining of western phosphate rock where weather conditions permit such mining only from 7 to 9 months during the year. Under such conditions, stockpiling and rehandling of rock are necessary to keep the processing plants in continuous operation. The over-all cost of this item is estimated at 25 cents per ton.

In the third step, the rock is crushed to a convenient size for subsequent grinding. The average cost of crushing is estimated at 20 cents per ton.

The fourth step is calcining the crushed rock to eliminate moisture and oxidize the organic matter, which causes some mechanical difficulties in the subsequent acidulation of the rock. This is usually done in a multiple-hearth furnace. The over-all cost of this step under present conditions is estimated at \$1.00 per ton. Where the rock contains very little organic matter, this step may not be necessary.

In the fifth step, the calcined rock is finely ground (99 per cent through a 100-mesh screen) to insure prompt and complete reaction between the

rock and sulfuric acid. The average over-all cost of grinding, including power, labor, and maintenance, is estimated at 40 cents per ton. This gives a total preparation cost of $6.35 per ton, exclusive of shipping charges.

Rock for Thermal Processes

The preparation of phosphate rock for the manufacture of phosphoric acid by thermal reduction methods involves at least three steps and in many cases a fourth, namely, mining, handing and storing, crushing and sintering or nodulizing.

Since the number and thickness of phosphate strata (such as siliceous phosphatic shales) adaptable to treatment by this method are far greater than those of high-grade rock, the cost of mining should be appreciably lower. Here, again, mining costs are influenced by the character of the deposits. Where strip mining is feasible, production costs are greatly reduced because of the large volume of rock that can be handled without the necessity of tunneling and timbering. Under most favorable conditions a cost of $1.00 per ton is possible, but as an over-all average the cost of mining the lower grade rock is estimated at $3.00 per ton, or about two-thirds that of high-grade rock. On the other hand, the phosphorus pentoxide content of furnace rock is only about 25 per cent, as against 33 per cent for high-grade phosphate. On this basis the average cost of mining the unit of phosphorus pentoxide is only slightly less for the lower grade material.

The second step, or unloading and crushing of the lower grade rock, should be approximately the same as that of high grade rock, namely, 20 cents per ton.

The fourth step, sintering or nodulizing may be unnecessary where phosphatic shales of the proper composition are available in lump form. Many of these phosphatic shales, however, are soft or friable and tend to disintegrate on mining. Moreover, a certain amount of blending of several strata may be required to obtain a properly proportioned furnace charge. Under such conditions the sintering or nodulizing of a large part of the material is required; the over-all cost of this is not less than $2.00 per ton, which may more than offset the saving effected in mining the lower grade phosphates.

Table 1 gives the estimated capital investment in storage and processing facilities and the relative costs of mining and preparing the rock for treatment by these two methods, per ton of material, as well as in terms of phosphorus pentoxide. Although the estimated total cost of the sintered or nodulized phosphate charge ready for furnacing is $0.90 less per ton than of rock for acid treatment, the cost of phosphorus pentoxide per ton in the former is $2.38 per ton higher.

Figure 2 shows, in diagrammatic form, various total costs of phosphorus

Table 1. Estimated Cost of Preparing Phosphate Rock for Treatment by Sulfuric Acid and Thermal Reduction Methods

(Capital investment—storage and processing equipment—$650,000)

	Rock for Sulfuric Acid Treatment (33% P₂O₅)		Rock for Thermal Reduction Method (11% P or 25.2% P₂O₅)	
	Cost per ton of rock	Cost per ton of P₂O₅	Cost per ton of rock	Cost per ton of P₂O₅
Mining, over-all cost..........	$4.50	$13.64	$3.00	$11.90
Processing costs				
Handling and storing........	0.16	0.49	0.16	0.63
Crushing....................	0.13	0.39	0.13	0.51
Grinding...................	0.26	0.79		
Calcining..................	0.65	1.97		
Nodulizing or sintering......			1.51	6.00
Depreciation (over-all), 7.5%	0.47	1.42	0.47	1.87
Insurance and taxes, 3.0%...	0.18	0.55	0.18	0.72
Total processing cost....	$1.85	$ 5.61	$2.45	$ 9.73
Grand total.............	$6.35	$19.25	$5.45	$21.63
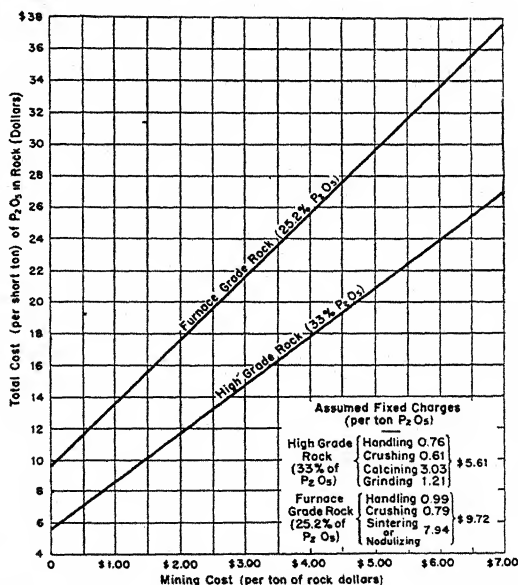
Figure 2. Comparative costs of P₂O₅ in high-grade phosphate rock ready for acid treatment and in low grade rock ready for smelting in the electric or blast furnace.

pentoxide in high-grade phosphate rock (33 per cent P_2O_5) ready for treatment with sulfuric acid, as well as the costs of phosphorus pentoxide in low-grade sintered or nodulized rock (25.2 per cent P_2O_5) prepared for the electric or blast furnace. In order to have equivalent costs per unit of phosphorus pentoxide in the two types of rock, it is evident that furnace-grade phosphate must be mined much more cheaply than that which is acidulated. As a specific example, where the cost of mining high-grade phosphate is \$4.50 per ton, low-grade rock must be mined for less than \$2.50 to give the same cost per ton of phosphorus pentoxide.

Reagents and Energy Required.

The relative costs of reagents and energy required in converting phosphate rock into phosphoric acid is a major factor in selecting the process for any particular locality.

In treating high-grade rock by the wet process to recover a ton of phosphorus pentoxide in the form of crude phosphoric acid, 2.57 tons of sulfuric acid (basis 100 per cent H_2SO_4) are required. The price of sulfuric acid varies widely, depending on its source and the distance it must be transported to points of consumption. Since smelter acid is a by-product, manufacturing charges depend largely on how the costs of preparing and treating metalliferous concentrates are distributed between the smelter and the acid plant.

In the electric-furnace modification of the thermal reduction method the main reagent (the one showing the widest variation in price) is electric energy. The power required to decompose furnace-grade phosphate rock for the recovery of one short ton of phosphorus pentoxide in the form of elemental phosphorus amounts to 5760 kw-hours, and the cost in the western area may range from 2 to 4.5 mills per kw-hour, depending on its source*. Two additional reagents (coke and carbon electrodes) are also required; the cost of these must be added to that of the power consumed. The quantity of coke for reducing purposes is approximately 0.61 ton, and the electrode consumption amounts to 16.4 pounds per ton of phosphorus pentoxide produced in the form of elemental phosphorus.

In the blast-furnace modification of the thermal reduction method, coke for both fuel and reducing purposes is the main reagent. The amount required per ton of phosphorus pentoxide produced is about 2.36 tons, and the delivered cost varies considerably depending on the distance it must be shipped.

Table 2 compares energy costs for phosphoric acid by alternate processes. In column 1 of Table 2 various energy costs per ton of phosphorus pentoxide in the form of phosphorus and phosphoric acid are assumed,

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* In Florida the cost of power is considerably higher.

and in columns 2, 3, and 4, prices are given at which sulfuric acid (per ton), fuel coke (per ton), and electric power (per kw-hour) must be obtained to yield the amount of energy required at equivalent cost. As a specific example, energy costing $20.56 per ton of phosphorus pentoxide
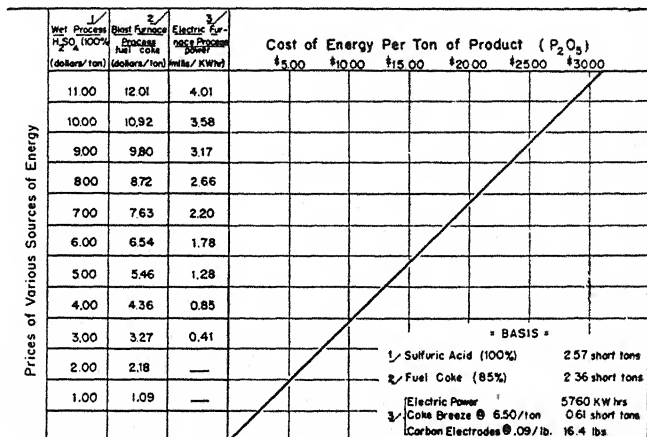
FIGURE 3. Equivalent costs of energy and reagents required in the manufacture of phosphoric acid (P_2O_5) by alternate methods.

TABLE 2. COMPARISON OF ENERGY COSTS FOR PHOSPHORIC ACID (P_2O_5) PRODUCTION BY ALTERNATE METHODS

Assumed Energy Costs, 1 Ton P_2O_5 as H_3PO_4 or Elemental P	Equivalent Cost of Energy Employed for Producing P_2O_5 from Phosphate Rock		
	Wet Process[a] (Product = H_3PO_4)	Blast-Furnace Process[b] (Product = Elemental P)	Electric-Furnace Process[c] (Product = Elemental P)
Dollars/ton	Sulfuric acid (100%), dollars/ton	Coke (85% C), dollars/ton	Electric power, mils/kw -hr
$5.14	$2.00	$2.18	. . .
7.71	3.00	3.27	0.40
10.28	4.00	4.36	0.84
12.85	5.00	5.46	1.29
15.42	6.00	6.54	1.73
17.99	7.00	7.63	2.18
20.56	8.00	8.72	2.61
23.13	9.00	9.80	3.07
25.70	10.00	10.92	3.52

[a] Basis, sulfuric acid (100%) = 2.57 short tons.
[b] Basis, coke (85% C) = 2.36 short tons.
[c] Basis, electric power = 5760 kw-hr; coke at $6.50 = 0.61 short ton; and electrodes at $0.09 per pound = 16.4 pounds.

can be delivered by sulfuric acid at $8.00 per ton, by coke at $8.72 per ton, or by electric power at 2.61 mills per kw-hour. The figures showing the equivalent cost of electric power are not strictly correct, since a constant price for coke breeze ($6.50 per ton) is assumed throughout. Any increase or decrease in the cost of this breeze will alter slightly the price that the manufacturer can afford to pay for electric power.

Figure 3 which gives this same data in diagrammatic form, enables one to estimate the relative economies of the reagents required by the various processes for any given locality.

Selection of Plant Site

Because the cost of the reagents and sources of energy required by these methods depend largely on where the phosphoric acid is manufactured, the site of the plant is a matter of great importance. Moreover, a plant site well adapted for one method may be entirely unsuitable for another.

In the wet process the cost of shipping the sulfuric acid required is considerably greater than that of transporting high-grade phosphate rock, and unless pyrites or sulfur can be delivered at a price permitting the economic production of sulfuric acid at the phosphate mines, construction of the phosphoric acid plant near the potential sources of cheap sulfuric acid is the logical course.

An electric-furnace plant, on the other hand, should be located close to the source of phosphate rock, since the cost of shipping this raw material, particularly the lower grades adapted to furnace treatment, is much greater than the cost of transmitting the electric power required an equal distance.

The same conditions apply to the blast-furnace modification of the thermal reduction method, since the quantity of coke employed is only half as great as that of the phosphate material required.

The following economic analysis is based on the assumption that a wet-process plant having an annual capacity of 33,000 tons of phosphorus pentoxide (53,400 tons of 85 per cent H_3PO_4) is situated at Salt Lake City, Utah, close to a source of smelter acid and that the thermal reduction plants (electric and blast furnaces) of equal capacity are situated at or near the phosphate deposits in southeastern Idaho[13].

Capital Investments

Because of the great advance and continual change in the cost of labor, structural materials, and equipment, the capital investment required and operating costs of a new plant are difficult to determine. Some of the figures given in the tabulated data, therefore, are necessarily estimated though based on known or published data; liberal factors have been applied to take care of the advance in prices.

In general, however, the capital investments involved and labor costs have been increased 150 per cent over those prevailing prior to the war, and though the figures admittedly are not strictly accurate they should not greatly affect the comparison of the two methods of producing phosphoric acid since fluctuations in prices affecting one method also apply to the other.

Manufacturing Costs

Sulfuric Acid Method

In estimating the cost of producing phosphoric acid by this method, the leading consultant and designer in this field was approached as to the present cost of a plant capable of producing 33,000 tons of phosphorus pentoxide in the form of concentrated acid (85 per cent H_3PO_4). Production of acid of this concentration involves the evaporation of large quantities of water; this is neither necessary nor desirable where triple superphosphate is the final product. Figures on labor, maintenance, and depreciation were also furnished, based on actual operation, and these have been modified to some extent to conform to the increase in the price of certain items[14].

The capital investment required for a plant of this size under present conditions is estimated at $1,810,000, exclusive of crushing and grinding facilities, or about 46 per cent that of an electric furnace phosphoric acid plant and about 30 per cent of the cost of a blast furnace phosphoric acid plant of equal capacities.

The labor required to operate a wet-process plant is considerably less than for either the electric- or blast-furnace method and the recovery of phosphorus pentoxide in the form of crude phosphoric acid is appreciably higher. Only one reagent (sulfuric acid) is required for the decomposition of the rock, and no temperatures higher than those furnished by steam are involved. If the phosphoric acid plant is built adjacent to a contact sulfuric acid unit, the steam obtained as a by-product in the latter is adequate for the evaporation of the phosphoric acid.

The cost of sulfuric acid obtained as a by-product in the smelting of metalliferous ores has been variously estimated at from $3.00 to $8.00 per ton. In the present estimate a price of $6.50 is assumed as conservative for a long-range program where the acid employed is largely a by-product.

The estimated cost of manufacturing phosphoric acid based on a plant erected near Salt Lake City, Utah, and employing by-product sulfuric acid, is given in Table 3. No equipment or costs for purifying this crude acid, however, are included in this estimate, and no credits are assumed for possible by-products, such as vanadium and fluorine compounds.

It should be emphasized that purification of the phosphoric acid produced by the wet process is both tedious and costly. Such acid contains

iron, aluminum, fluorine, lead, and arsenic, all of which must be removed to render the product suitable for food and most chemical uses. Partial

TABLE 3. ESTIMATED COST OF PRODUCING P_2O_5 AS PHOSPHORIC ACID (85% H_3PO_4) BY SULFURIC ACID PROCESS (DORR STRONG ACID SYSTEM)

Capital investment

Real estate	$	10,000
Buildings		500,000
Equipment		1,300,000
Total		$1,810,000

| | Unit Cost | Per Ton of Product[a] | | | | % of Total Cost |
| | | P_2O_5 | | H_3PO_4 (85%) | | |
		Quantity	Cost	Quantity	Cost	
Raw materials						
Phosphate rock (33% P_2O_5), short ton..............	$7.81[b]	3.23	$25.23	1.99	$15.54	53.96
Sulfuric acid (100% H_2SO_4), short ton..............	6.50	2.57	16.70	1.59	10.33	29.23
Total for materials.......		5.80	$41.93	3.68	$25.87	73.19
Conversion						
Power, kw-hr..............	0.0025	115	$ 0.29	71.0	$ 0.18	0.50
Labor, operating supervision			2.65		1.64	4.64
Labor, maintenance........			2.00		1.23	3.48
Labor, laboratory and office.			0.75		0.46	1.30
Evaporation, steam per ton.	1.05[c]	1.87	1.96	1.15	1.21	3.43
General plant expense......			0.44		0.27	0.76
Maintenance, materials.....			1.50		0.93	2.63
Depreciation (over-all), 7.5%			4.11		2.54	7.19
Insurance and taxes, 3%....			1.65		1.02	2.88
Total for conversion......			$15.35		$ 9.48	26.81
Grand total.............			$57.28		$35.35	100.00

[a] Based on recovery of 94% of the P_2O_5.

[b] Including freight to Salt Lake City, Utah.

[c] Per ton steam derived from average coal at $5.00 per ton, assuming efficiency of 50%.

neutralization of the acid with lime is necessary to eliminate some of these impurities; this results in the formation of phosphate precipitates that are difficult to market. Additional filtrations and washing are necessary, and the partially neutralized solution must be reacidulated with pure sulfuric acid, concentrated, and again filtered free of calcium sulfate. The fact

that many of those previously used pure phosphoric acid manufactured by the wet process now employ acid derived from the electric furnace method, is rather conclusive evidence that the latter acid is more satisfactory and probably more economical for food and high-grade chemical products. The logical use for phosphoric acid produced by the sulfuric-acid method is in the manufacture of fertilizer materials in which purity is not essential.

Electric-Furnace Process

Whereas the electric-furnace process has been modified and improved during the past decade[13] there is still opportunity for further simplification and economic development. As conducted today, this process involves two broad steps; in the first step the properly prepared phosphate charge (mixed with coke breeze) is smelted in an oblong three-phase electric furnace and the elemental phosphorus reduced, volatilized and collected as described in Chapter 10. The second step involves feeding liquid phosphorus through a special burner to a combustion chamber wherein it is oxidized with an excess of air to produce phosphorus pentoxide. The latter compound is then hydrated and collected as strong phosphoric acid by means of a Cottrell electrical precipitator as described in Chapter 11.

The equipment for converting elemental phosphorus into phosphoric acid has been so improved and simplified in recent years that in spite of the advance in the prices of labor and material of construction, the cost of a modern plant should not be greatly in excess of that of the more elaborate type previously employed. The capital investment in this new type of plant for producing 33,000 tons of P_2O_5 per annum in the form of concentrated phosphoric acid is estimated at $500,000. A power rate of 2.5 mills per kw-hour has been assumed and the costs of labor and materials are estimated at 150 per cent above those prevailing prior to World War II. On this basis, the detailed costs of manufacturing phosphoric acid from elemental phosphorus produced by the electric-furnace process are given in Table 4.

Blast-Furnace Process

Provided the phosphorus collected in the blast-furnace process is relatively pure and can be handled in liquid form, the cost of converting it into phosphoric acid is the same as that of manufacturing this acid from electric furnace phosphorus. Any difference in the cost of phosphoric acid produced by these two modifications of the thermal reduction method of treating phosphate rock lies in the cost of manufacturing the elemental phosphorus[13].

Referring to the estimates given in Tables 5 and 6 of Chapter 10, the cost of elemental phosphorus per ton obtained by the electric-furnace process is $151.89 as against $164.21 per ton for that produced through the medium of·the blast furnace. On this basis the cost of manufacturing P_2O_5

TABLE 4. ESTIMATED COST OF MANUFACTURING P_2O_5 AS PHOSPHORIC ACID (85% H_3PO_4) BY COMBUSTION OF ELEMENTAL PHOSPHORUS PRODUCED BY ELECTRIC-FURNACE PROCESS

(Annual production for 330-day operation, 33,000 tons P_2O_5, equal to 53,600 tons 85% phosphoric acid)

Capital investment

Real estate	$ 10,000
Buildings	40,000
Equipment	450,000
Total	$500,000

	Unit Cost	Per Ton of Product				% of Total Cost
		P_2O_5		H_3PO_4 (85%)		
		Quantity	Cost	Quantity	Cost	
Phosphorus, short ton........	$151.89	0.446ᵃ	$67.74	0.276ᵃ	$41.93	91.93
Conversion						
Power.....................			$ 0.04		$ 0.02	0.04
Labor, operating and super- vision.................			1.51		0.93	2.03
Labor, maintenance........			1.27		0.78	1.70
Labor, laboratory and office.			0.54		0.33	0.72
Maintenance, materials.....			0.40		0.25	0.54
General plant expense......			0.30		0.19	0.42
Depreciation (over-all), 10%			1.48		0.92	2.01
Insurance and taxes, 3%....			0.46		0.28	0.61
Total cost...............			$ 6.00		$ 3.70	8.07
Grand total.............			$73.74		$45.63	100.00

ᵃ Based on 98% recovery.

in the form of concentrated phosphoric acid is $5.45 more per ton by the latter than by the former method. The cost of manufacturing phosphoric acid from elemental phosphorus derived from the blast-furnace process is given in Table 5.

According to the figures given in Tables 3, 4, and 5, the estimated cost of manufacturing phosphorus pentoxide (per short ton) in the form of phosphoric acid (unpurified) by the wet or sulfuric acid process, the electric

furnace method and the blast furnace method is $51.28, $73.74 and $79.19 respectively. These comparative itemized costs as well as those of the P_2O_5 in triple superphosphate produced from acid at the above prices are given diagrammatically in Figure 4.

TABLE 5. ESTIMATED COST OF MANUFACTURING P_2O_5 AS PHOSPHORIC ACID (85% H_3PO_4) BY COMBUSTION OF ELEMENTAL PHOSPHORUS PRODUCED BY BLAST-FURNACE PROCESS

(Annual plant capacity, 300-day operation, 33,000 P_2O_5 equal to 53,600 tons 85% H_3PO_4)

Capital investment

Real estate	$ 10,000
Building	40,000
Equipment	450,000
Total	$500,000

	Unit Cost	Per Ton of Product				% of Total Cost
		P_2O_5		H_3PO_4 (85%)		
		Quantity	Cost	Quantity	Cost	
Phosphorus, short ton........	$164.11	0.446[a]	$73.19	0.276[a]	$45.29	92.44
Conversion						
Power......................			0.04		0.02	0.04
Labor, operating and super-vision.................			1.51		0.93	1.90
Labor, maintenance........			1.27		0.78	1.60
Labor, laboratory and office.			0.54		0.33	0.68
Maintenance, materials.....			0.40		0.25	0.51
General plant..............			0.30		0.19	0.38
Depreciation, 10%..........			1.49		0.92	1.88
Insurance and taxes, 3%....			0.45		0.28	0.57
Total for conversion......			$ 6.00		$ 3.70	7.56
Grand total..............			$79.19		$48.99	100.00

[a] Estimated recovery of 98%.

It will be noted that the largest items of expense in all these processes are the raw materials and the reagents required. Therefore any substantial change in these items will materially affect the cost of the final product. By use of the diagrams given in Figures 2, and 3, however, the cost of the raw materials and reagents can be adjusted to conform to particular conditions and enable those planning new developments to chose the process best adapted to a given locality.

FIGURE 4. Estimated cost of one ton P_2O_5 in form of phosphoric acid (85% H_3PO_4) and triple superphosphate (48% P_2O_5) produced by alternate processes.

It must be borne in mind that the cost figures apply to phosphoric acid that has not been purified. The purification of phosphoric acid manufactured from elemental phosphorus is comparatively simple compared to the elaborate procedure involved in purifying the crude acid obtained by the so-called wet process. Hence any price advantage which the latter may have over the acid derived from elemental phosphorus is more than offset by the cost of the additional purification steps required.

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14. Purification of Phosphoric Acid and Its Salts

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No matter how pure the raw materials used in its manufacture may be, phosphoric acid which is to be used for food and high-grade chemical purposes must be purified[9, 17]. On the other hand, phosphoric acid used in the manufacture of fertilizers need not be purified.

The procedure and number of steps required in the purification of phosphoric acid depend on the method employed in manufacturing the acid and the ultimate use of the products.

In thermal reduction processes which involve the reduction of phosphate to elemental phosphorus and its subsequent oxidation, the bulk of the nonvolatile impurities present in the rock are left in the residue or slag and with due precautions only very small quantities of silica, lime and iron and aluminum phosphates are carried over and condensed or dissolved in the acid collected.

If the so-called one-step modification of the thermal reduction process is employed, which comprises the simultaneous oxidation of the phosphorus vapor and combustible gases as they issue from the furnace, certain volatile impurities such as sulfur and its compounds, arsenic and fluorine compounds may be present in the acid. Since lead is often employed in some part of the collecting or storage equipment the acid must as a rule be treated to remove this impurity.

If however, the two-step process is used wherein phosphorus is removed from the furnace gases by condensation and subsequently burned in a separate combustion chamber, most of the volatile contaminants are eliminated and the resultant acid contains only minor quantities of impurities.

PURIFICATION OF PHOSPHORIC ACID

Where phosphoric acid is produced from phosphate rock by the sulfuric acid process, its purification and concentration entail considerable time

manipulation and expense. Such acid always contains a number of impurities which are objectionable for one or more of the following reasons:

(1) They reduce the acidity of the product.
(2) They render the products manufactured therefrom more difficult to handle.
(3) They yield products of poor color and of inferior grade.
(4) They cause certain products (baking powders) to have poor keeping qualities.
(5) They may render food products unwholesome or actually deleterious to health.

Silica and Calcium Sulfate

These are solid impurities obtained almost coincident with the treatment of phosphate rock with sulfuric acid—silica being present in the rock and calcium sulfate being formed in the reaction. The bulk of these contaminants is removed by filtration, but thorough washing of the residue with dilute acid and finally with water is necessary to leach out the phosphoric acid absorbed or contained therein. As pointed out previously, this loss in a properly operated plant should not exceed $1\frac{1}{2}$ per cent of the acid produced.

Owing to the solubility of calcium sulfate in relatively dilute phosphoric acid, an appreciable quantity (1 to 3 per cent) of this compound is held in solution, but is removed in subsequent treatment.

Arsenic and Lead

Some phosphate rocks contain appreciable quantities of arsenic and since this element, as well as its oxide, is quite volatile at elevated temperatures, small amounts may be found in the acid produced by the thermal reduction method (particularly when the one-step modification method is used).

If phosphate rock is decomposed with lead chamber sulfuric acid derived from the combustion of pyrites, the resultant phosphoric acid nearly always contains appreciable quantities of arsenic and lead. Both of these impurities must be reduced to mere traces before the acid can be used for food grade products.

Fortunately both lead and arsenic can be precipitated by passing hydrogen sulfide gas directly into the acid or by adding a soluble sulfide which is acted upon by the acid to form H_2S.

After the arsenic and lead are precipitated, the excess of hydrogen sulfide must be completely removed from the acid since the presence of this gas even in small quantities interferes with subsequent filtration. The colloidal sulfur that is formed tends to clog the filtering media. The excess

H_2S is driven off by heating the acid to at least 50°C and passing through it a stream of air or carbon dioxide gas.

Booth and Malowan[3] claim, however, that in the case of relatively concentrated phosphoric acid, lead is more effectively removed by having a small amount of free sulfuric acid present and then adding a soluble barium or strontium salt. The resultant precipitate is said to occlude lead compounds and remove them from solution. Woodstock[21] claims that very small additions of sodium iodide or bromide to phosphoric acid containing a little sulfuric acid facilitate the removal of lead, and Knox[14] found that the same effect could be obtained with strong phosphoric acid (70 per cent H_3PO_4 or higher) by addition of sodium chloride.

Hurka[13] states that on account of its viscosity, phosphoric acid having a concentration of 80 per cent H_3PO_4 or more cannot be readily freed from arsenic by means of hydrogen sulfide, but that if such acid is contacted with metallic copper the arsenic is precipitated probably as copper arsenide which does not dissolve in concentrated phosphoric acid, provided non-oxidizing conditions are maintained.

Fluorine

Phosphoric acid manufactured either by the one-step modification of the thermal reduction method or by the sulfuric acid process contains fluorine largely in the form of fluosilic acid or fluosilicates.

If the presence of sodium salts is not objectionable in the final product, the fluorine can be precipitated and filtered off as sodium fluosilicate by the addition of an amount of soda sufficient to convert 50 to 75 per cent of the acid into monosodium phosphate.

In manufacturing phosphoric acid from high-grade apatite (low in iron and aluminum) Ferney[6] states that the fluorine can be largely removed by adding sodium phosphate to the sulfuric acid used in the decomposition steps. The sodium fluosilicate resulting from this treatment is precipitated along with gypsum and subsequently removed by decantation or filtration. Any fluosilicates still remaining in solution are crystallized out when the acid is concentrated.

Carothers and Gerber[4] patented a process for removing fluorine from phosphoric acid by addition of either sodium silicate or sodium phosphate. Knox *et al.*[14a] proposed to remove fluorine by filtering the impure phosphoric acid through beds of hydrated silica, and Booth[2] has suggested absorption of the fluorine compounds by passing concentrated phosphoric acid through a column of skeletal silica. Hettrick[8] claims to reduce the fluorine content of such concentrated acid by blowing superheated steam through it at a temperature of 280°F.

When phosphoric acid contains substantial quantities of iron and

aluminum, as is the case where the acid is produced from the average grade of phosphate rock by the wet process, the fluorine may be removed along with these other impurities as described below.

Iron and Aluminum

These impurities are the most costly to remove from phosphoric acid since when precipitated they carry with them very appreciable quantities of phosphoric acid which is so combined that it cannot be recovered by leaching the precipitate with water or dilute acid.

The removal of these impurities is brought about by the addition of finely ground limestone to the acid. During the violent reaction which ensues the solution heats up and the large volume of CO_2 evolved carries off any residual H_2S which may still be in the acid.

This treatment with limestone produces a solution of monocalcium phosphate, a certain amount of dicalcium phosphate and precipitates iron and aluminum phosphates, calcium fluoride and fluosilicates. The free acidity of the resulting solution is reduced by this treatment to about 4.5 per cent.

This mixture of insoluble compounds is then removed from the acid solution of monocalcium phosphate by filtration. The residue has a high absorptive capacity for soluble salts and hence it is necessary to wash it thoroughly in order to reduce to a minimum the losses of soluble P_2O_5. The soluble phosphate in the wash water is often precipitated as dicalcium phosphate by the addition of lime, and this dicalcium phosphate in turn is filtered off, added to the monocalcium phosphate solution and reconverted into phosphoric acid as described below.

The monocalcium phosphate solution, after removal of the iron, aluminum and the bulk of the fluorine, is then mixed with pure sulfuric acid, and insoluble calcium sulfate thus precipitated and filtered off. The phosphoric acid thus obtained is nearly free from all objectionable impurities but since it seldom has a strength of over 30°Bé (40 per cent H_3PO_4), it must be concentrated before it is suitable for the market. This concentration is accomplished either in vacuum evaporators, by bubbling large volumes of hot gas through a column of the liquid, or spraying the acid into a chamber countercurrent to a stream of such gases. During the concentration process, any residual fluorine compounds still present in the acid are driven off as hydrofluoric acid and crystals of calcium sulfate settle out.

Hickson[9a], claims that phosphoric acid may be economically freed from metallic contaminants (Fe, Al, and Pb) by addition of a large volume of glacial acetic acid. After the mixed precipitates are removed by filtration, the acetic acid is recovered from the phosphoric acid solution by distillation.

Coleman[6] has proposed a method of producing pure phosphoric acid consisting in mixing phosphate rock with an amount of phosphoric acid approximately sufficient to form monocalcium phosphate, heating the resultant mass to a temperature below 240°C to convert it largely into metaphosphates and treating the dried product with phosphoric acid to reconvert it into orthophosphate. Sufficient sulfuric acid is then added to precipitate the lime and produce an equivalent quantity of phosphoric acid. It is claimed that the iron and aluminum metaphosphates produced during the dehydration step do not dissolve again when treated with phosphoric and sulfuric acids and are thus readily separated from the final product.

Low[16] claims much the same result by heating crude phosphoric acid above 300°C until the iron and aluminum are converted into insoluble metaphosphates. The acid is then diluted and these impurities removed by filtration. Other troublesome contaminants such as fluorine, arsenic and sulfur (as SO_3) are said to be volatilized during the heating step.

Vanadium

The phosphate rock of the western states contains appreciable quantities of vanadium which dissolves when the rock is treated with sulfuric acid, imparting a green color to the resulting phosphoric acid and to products derived therefrom. To remove vanadium, Laist[15] first proposed to treat phosphoric acid with a sufficient quantity of sodium ferrocyanide to precipitate all of the vanadium and most of the iron. The precipitate was then filtered off, digested with sodium hydroxide, and the sodium ferrocyanide regenerated to be used over again. The vanadium in the residue was then recovered as a by-product.

The method now used for removing vanadium from wet-process acid consists in adding sodium chlorate to the filtered acid (after concentrating it to 53°Bé). The oxidizing agent ($NaClO_3$) causes the precipitation of phosphovanadic acid which is subsequently separated and purified for market[18].

Phosphoric acid manufactured by thermal reduction methods contains no vanadium since this element is largely reduced and retained in the ferrophosphorus formed in the furnace.

Decolorizing

Crude phosphoric acid produced by the sulfuric acid method is highly colored due partly to the presence of dissolved organic matter, and partly to the presence of very small quantities of chromium, vanadium and molybdenum compounds. Organic contamination may be greatly reduced by calcining the phosphate rock before converting it into phosphoric acid and taking proper precautions to avoid fouling the solutions with oil, pump

packing, etc. Organic discoloration, however, may be readily destroyed by oxidation and such oxidizing agents as permanganates, chlorates and chlorine gas[11] have been used for this purpose.

Coloration due to the presence of the rarer metals mentioned above is not as easily eliminated, but is corrected to a large extent by means of oxidizing agents. Ferney[7] states the higher oxides of these metals (V_2O_5, CrO_3, and MoO_3) are almost colorless, except in the presence of chlorides. Therefore, he recommends the use of permanganates rather than chlorates or perchlorates as oxidizing agents.

The acid produced by thermal reduction methods should be free from organic impurities provided collecting equipment, pumps, pipelines and storage facilities are kept clean.

Crystallized Phosphoric Acid

Theoretically the ideal way to obtain phosphoric acid absolutely free from all impurities is to crystallize this compound, but while this has been done in a relatively small way the method has not as yet been applied on a commercial scale.

Ross, *et al.*[19] described a process for purifying phosphoric acid which may be briefly outlined as follows:

Phosphoric acid (produced by the volatilization process) is brought to a specific gravity of 1.85 either by dilution with water or by evaporation, care being taken that the acid solution is not heated above 150°C. The acid is then cooled to 20°C and inoculated with a crystal of H_3PO_4, whereupon the whole mass solidifies. The crystalline mass is then centrifuged and the crystals separated from the mother liquor and dried. The dried crystals are nearly free from impurities, but if it is desired to purify them still further, a little water may be added and the process repeated. The mother liquor may be used over again in the cycle or employed directly for the manufacture of products where highly purified acid is not so essential.

A modification of this method of purification described by Carothers and Gerber[5] is said to be particularly applicable to acid produced by thermal reduction processes. The method consists in first treating acid having a concentration of over 82 per cent of H_3PO_4 with sodium sulfide and silicate of soda to remove the arsenic and fluorine compounds. The suspended matter is then allowed to settle and the acid filtered, aerated at 50°C to remove volatile matter, cooled to 10°C and inoculated with a crystal of phosphoric acid. The mass of crystals formed under these conditions is then separated from the mother liquor by centrifuging.

Ross, *et al.*[20] showed that phosphoric acid produced by the volatilization process when crystallized has a purity superior to that which has been put

through elaborate chemical treatments. These investigators also worked out a chart showing the solubility of both anhydrous and hydrated crystalline phosphoric acid, which should be of considerable value as a means of determining the yield of two types of crystals under varying conditions of concentration and temperature. This chart (Figure 1) and their description of its use are given below.

"The solubility curve AB of anhydrous phosphoric acid and that portion CDE of the curve of the hydrated acid above 15°C are represented
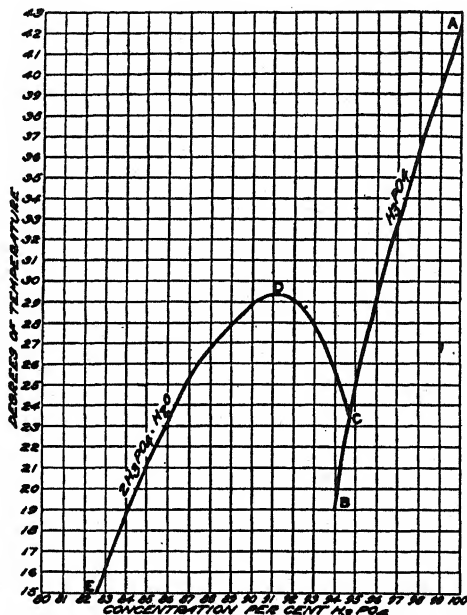
FIGURE 1. Solubility curves of hydrated and anhydrous orthophosphoric acid.

in the figure. By use of these curves the amount of acid that will be deposited on crystallizing from a solution of known concentration and temperature may be readily estimated. Thus at 24°C, for example, no crystallization will occur below a concentration of 86.3 per cent. Above this concentration a hydrated crystal will induce partial crystallization in the solution, the proportion increasing up to 91.6 per cent when the whole mass becomes solid. With still greater concentrations partial crystallization again occurs until at a concentration of 94.6 per cent no crystallization follows inoculation with either hydrated or anhydrous crystals. This holds true up to 94.8 per cent acid. Above this concentration partial crystallization follows inoculation with either hydrated or anhydrous crystals. The amount

deposited increasing up to 100 per cent when it crystallizes to a solid mass. The curves also show that at 24°C no crystallization will take place when a 94.8 per cent solution is inoculated with either a hydrated or anhydrous crystal or both, but that the whole mass becomes solid when the temperature of the solution is lowered one degree more."

Unfortunately for this method of purifying phosphoric acid, the temperature to which the acid is subjected before crystallization has a marked effect on the rate at which crystallization takes place, and according to the authors just cited, acid which has been maintained at a temperature of 130°C or above for a protracted period will not crystallize. This practically precludes employing the crystallization method for purifying phosphoric acid manufactured by the sulfuric acid process.

Pure Sodium Phosphate Salts from Wet Process Phosphoric Acid*

In producing high-quality sodium phosphate salts from wet-process acid, it is not customary to resort to prior treatment of the acid to produce a complete or semi-purification. A satisfactory elimination of the major impurities can be accomplished at various stages of neutralization by proper treatment. As rather voluminous precipitates result in some of the neutralization steps it is necessary to start with phosphoric acid of not over 20 to 25 per cent P_2O_5 content for efficient filtration and handling. Concentration of the neutral liquors to salt out the impurities cannot be resorted to, due to the high loss of P_2O_5 that accompanies salting out operations.

In addition to mineral impurities, wet phosphoric acid produced from raw rock will be highly colored due to the action of the sulfuric acid on the organic constituents. This color persists through all neutralization and purification steps giving a definite off-color to crystals produced unless they are thoroughly washed. The generally adopted procedure to overcome this difficulty is to calcine the rock prior to acid digestion. Prepared or calcined rock is available from the Florida deposits. Users of western phosphate rock in the United States calcine the rock prior to use to reduce the foaming during acid digestion and this step is followed by European manufacturers using north African rock .

The major portion of the H_2SiF_6 (fluosilicic acid) content of the phosphoric acid produced can be removed by partial neutralization to monophosphates with soda ash or di-soda liquor[10, 12], within a neutralization range of 10 to 20 per cent. A coarse granular precipitate of Na_2SiF_6 will result from this partial neutralization and can be removed by filtration, washed, dried and disposed of as commercial sodium silicofluoride. The purity of the product depends upon the clarity of the phosphoric acid and

* W. T. Grace, Grasselli Chemicals Dept., E. I. du Pont de Nemours & Company.

with clear acid will approximate 98 to 99 per cent Na_2SiF_6, the major contaminant being P_2O_5. The removal of fluorine will not be complete by the above procedure but the small amount remaining in solution can be readily removed in a subsequent neutralization step.

The lead and arsenic are removed from the defluorinated acid by treatment with sodium sulfide liquor. The reaction is slow and a retention period after the sulfide treatment will lead to more complete precipitation. The precipitate will not be of any great volume and a treatment for reduction of the sulfate content can be carried out in the presence of the lead and arsenic sulfides.

Sulfates can be reduced to small amounts by slow treatment of the liquor with barium carbonate until a test shows a slight amount of soluble barium in the acid liquor. The arsenic and lead sulfides and barium sulfate should be removed by filtration at this point.

The acid filtrate at this point contains the iron and alumina originally present in the acid, a small amount of fluorine and traces of barium. Neutralization by addition of soda ash to pH 4.0 to 4.2 will precipitate the iron and alumina as phosphates and the remaining fluorine as sodium aluminum fluoride. Before filtration, the heating of the slurry to 210°F with live steam will drive out all CO_2, convert the soluble barium to insoluble barium phosphate and condition the heavy slurry for filtration. This is the most voluminous precipitate obtained in any of the purification steps and contains from 8 to 15 per cent of the P_2O_5 originally in the acid as insoluble iron and aluminum phosphates. The filter cake may be thoroughly washed to recover all soluble P_2O_5 and then dried and disposed of as an ingredient for mixed fertilizer goods.

The filtrate obtained at this point is suitable for the production of monosodium phosphate crystals by concentration of the liquor and crystallization. Limited crystal crops may be required for highest purity products and mother liquors may have to be diverted to di-soda production. Monosodium phosphate crystals produced from liquors of pH 4.0 to 4.2 may be converted to acid pyrophosphate by further dehydration in high-temperature ovens or rotary calciners.

Mother liquors from monosodium phosphate operations or monosodium liquors from the previous soda ash neutralization or mixtures of the two may be further neutralized to disodium phosphate by soda ash addition to pH 8.6 using phenolphthalein as an indicator. This induces a small additional precipitate of iron and aluminum phosphates requiring another filtration step but yields a di-soda liquor with lower fluorine content than direct neutralization of the phosphoric acid to the di-soda stage with no intermediate filtration.

FIGURE 2. Flow sheet showing manufacture of high-quality sodium phosphate salts from wet process phosphoric acid.
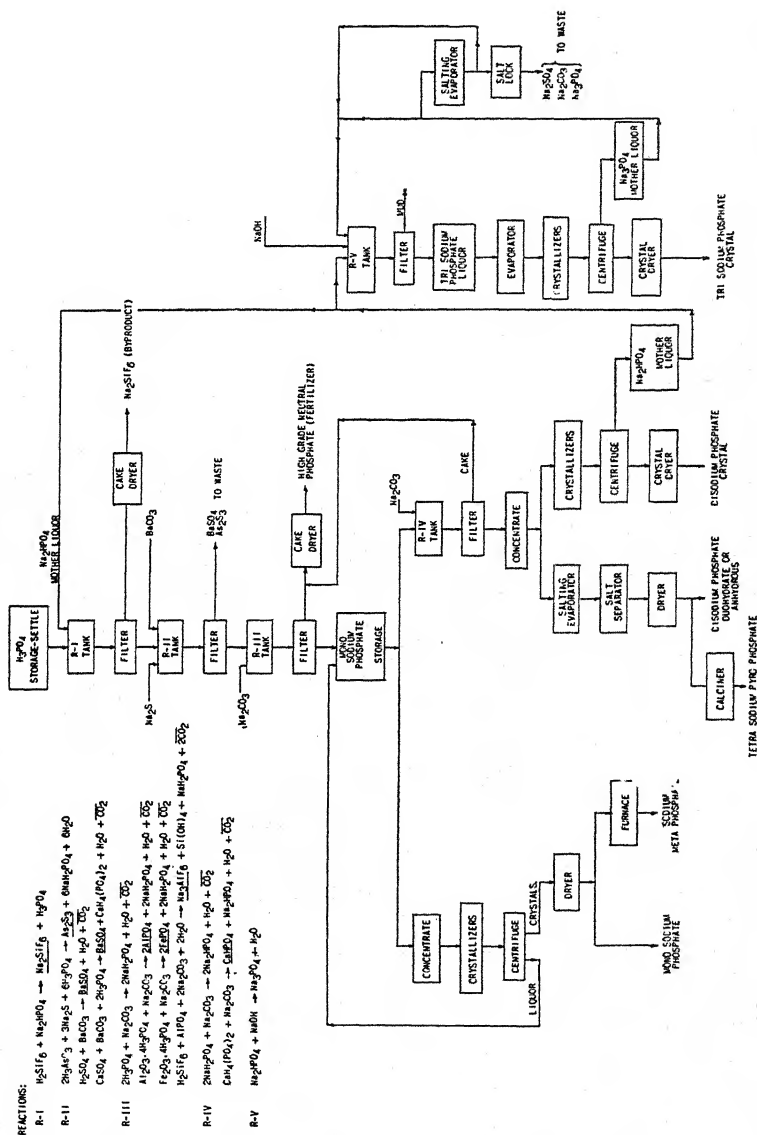
After concentration of the filtrate, disodium phosphate crystals may be produced in cooler-crystallizers with separation of the mother liquor in the usual manner. Concentration and salting out in an evaporator may be resorted to and with proper adjustment of temperature conditions either the duohydrate crystal or anhydrous crystal may be obtained. Any of the above products may be treated in direct fired rotary calciners to produce sodium pyrophosphate.

This removal of di-soda crystals from the liquor results in an increase in the ratio of impurities to remaining di-soda content and this ratio can be brought back to normal by return of the di-soda mother liquors to the first neutralization step to precipitate the sodium silico fluoride, whereupon the impurities will be reduced to normal in the subsequent purification steps.

A further purge of the impurities in the di-soda circuit can be accomplished by diversion of a constant amount of the mother liquors to a trisodium phosphate circuit. This product is not used as a constituent of food products and the tolerances or impurities permitted are more lenient.

Virgin di-soda liquor or mixtures with di-soda mother liquor are treated with caustic soda to a small excess of free NaOH. This may result in a turbid liquor if iron and manganese are present and a clarification filtration may be found necessary. The end product liquor of trisodium phosphate can then be concentrated as required for delivery to a water-cooled crystallizer to produce Na_3PO_4, $12H_2O$ crystals with separation of the mother liquor for return to the caustic neutralization step.

For the production of a-flake or pelleted product, the TSP liquor may be concentrated to crystal strength and fed to a water-cooled flaking roll or sprayed into a cooling chamber.

When large proportions of crystal TSP are being produced the impurities may build up in the mother liquors to such an extent that satisfactory crystal crops are not obtained. This build-up of sodium sulfate, chloride and carbonate may be eliminated by periodic evaporation of the mother liquors to very high concentration in a salting-out evaporator and the salt lock content consisting of sodium sulfate, carbonate, chloride and phosphate discarded.

By careful control of conditions, limitation of the crystal crops removed and careful washing of crystals to remove adhering mother liquor, it is possible to produce mono- and disodium phosphate products that meet the specifications of the U. S. Pharmacopia and Food and Drug requirements.

A typical flow sheet of wet-process soda salts production with the main reactions involved is shown in Figure 2.

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15. Superphosphate, Its Manufacture and Properties

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Superphosphate is a term generally applied to the product obtained by treating finely ground bones or phosphate rock with sulfuric acid. Whereas, a number of chemical changes take place between the acid and the various minerals in phosphate rock, the main reaction sought and the one of prime importance from an agricultural standpoint is the conversion of the insoluble tricalcium phosphate (usually present as fluorapatite) into monocalcium or a readily soluble phosphate salt and calcium sulfate. The various reactions involved in the manufacture of superphosphate are discussed later in this chapter.

Superphosphate was the first chemically prepared fertilizer product and marked the evolution of a relatively small haphazard business into an immense industry involving the application of scientific knowledge and sound engineering principles.

HISTORICAL

There has been considerable controversy as to who first discovered the process of acidulating natural phosphates in order to render them more quickly available to crops. About 1934, however, the International Superphosphate Association instigated an inquiry to determine definitely the names of investigators responsible for this epoch-making development[21, 24].

The results of this investigation established the fact that in 1835 a German named Escher first suggested the acidulation of finely ground bone meal to render it more effective as a fertilizer. Escher, however, died before he actually conducted any extensive experiments along these lines.

In 1839 to 1840, Leibig, who apparently knew nothing of Escher's work, published a report in which he said good results could be obtained by

treating plants with acidulated bone. Leibig did not patent this process but in 1845 he took out a patent for mixing acidulated bone with carbonates of lime, potash and soda. In view of Leibig's knowledge of chemistry it is rather surprising that he should have proposed such a process as the addition of these alkaline salts only served to revert the phosphate to less soluble forms.

In 1842, J. B. Lawes[14] was issued a patent covering the acidulation of phosphate rock. Subsequently, he admitted that Leibig had priority on the process of acidulating bone products and hence amended his patent to cover only phosphate minerals. Lawes made a commercial success of his discovery and is generally regarded as the father of the superphosphate industry, although Packard states that his grandfather, Edward Packard, erected the first complete superphosphate factory in 1854[21].

The superphosphate produced in these early days was irregular in composition and often in poor physical condition due to the following causes:

(1) An incomplete understanding of the action of sulfuric acid upon the various impurities occurring in natural phosphates, and the consequent lack of chemical control over the raw materials entering into the manufacture of superphosphate.

(2) The limited knowledge of the importance of sulfuric acid concentration upon the rate and thoroughness of the chemical reactions and the mechanical condition of the product.

(3) The use of coarsely ground phosphates which were incompletely attacked by sulfuric acid.

(4) The employment of hand labor in mixing the acid and rock which made it impracticable to obtain the intimate contact necessary for rapid and complete reaction.

(5) The dumping of the freshly prepared material upon open piles almost immediately after mixing, a practice which so cooled the mass that the chemical reactions were checked and the moisture content of the product was objectionably high.

The importance of certain factors in acidulating phosphates was soon recognized and resulted in more economical and efficient methods being introduced. Today accurately proportioned charges of phosphate rock and sulfuric acid, the composition and strength of which are definitely known, have replaced the loose approximations of the early days. Fertilizer machinery for grinding, mixing, curing and disintegrating materials has reached such a high degree of perfection that there is no longer any excuse for incompletely acidulated phosphates due to improper grinding or mixing of the raw materials, nor any reason for undue delay in curing and shipping superphosphate for lack of the proper mechanical facilities. But while the mechanics of this process have been pretty thoroughly worked out,

and a better understanding of the chemical nature of the product gained[7, 8, 9, 10, 16, 17], there still appears to be room for further research. It is reasonable to expect that continued investigations will lead to economies in acid consumption, resulting in the production of more concentrated superphosphate and a better utilization of our phosphate resources.

Owing to the fact that finely ground steamed or degreased bone is more valuable as an animal feed supplement, and also because water-soluble phosphates can be obtained so much more readily and cheaply by the acidulation of mineral phosphates, the percentage of bone products now treated with sulfuric acid is very small.

In manufacturing soluble phosphates for fertilizer purposes from degelatinized bone, the bones are first ground to pass at least a 60-mesh sieve and then treated with an equal weight (approximately) of 60 per cent sulfuric acid or its equivalent in more concentrated acid. The mass is thoroughly mixed and allowed to cure until the chemical reactions are practically complete. Dissolved bone contains in addition to water-soluble phosphate a small amount of fixed nitrogen also in an available condition, which adds to its agricultural value. The main fertilizer ingredient, however, is monocalcium phosphate and the amount of water-soluble phosphoric acid (P_2O_5) in this form varies between 15 and 20 per cent, depending on the type of bone used and the concentration of the acid employed in decomposing it. Unfortunately the character and quantity of the organic matter in some of the bone used is such that upon treatment with sulfuric acid a viscous mass results which is difficult to dry. This objection does not apply, however, to bone char and bone ash, both of which are used to a limited extent in the manufacture of water-soluble phosphates.

The vast bulk of soluble phosphate produced both in this country and abroad, however, is manufactured from the amorphous phosphates of lime, deposits of which have been previously described. The general procedure followed in making superphosphate is a familiar one, and most of the larger manufacturers of this commodity exercise great care in its preparation, checking both the raw materials and finished product by chemical analyses and endeavoring by the use of the most modern equipment to obtain a superphosphate of the highest concentration and availability and in the best possible mechanical condition for distribution in the field.

Although other types of water-soluble phosphates such as ammonium phosphates, triple-superphosphate and double salts of phosphoric acid have gained in favor, ordinary superphosphate continues to be the chief carrier of P_2O_5 in fertilizers.

Table 1 shows the annual production of superphosphate in the United States from 1939 to 1949 inclusive. An aerial view of the largest superphosphate plant in the United States is shown in Figure 1.

Some of those engaged in the production of this material, have a rather limited knowledge of the chemistry involved and are not too familiar with

TABLE 1. U. S. PRODUCTION OF ORDINARY SUPERPHOSPHATE (18% P_2O_5 BASIS)
Short Tons (1939–1949)

Year	Production (Tons)
1939[a]	3,514,400
1940[a]	4,024,400
1941[a]	4,493,900
1942[a]	5,144,484
1943[a]	6,294,665
1944[b]	6,692,368
1945[b]	7,372,104
1946[b]	7,847,591
1947[b]	9,292,677
1948[b]	9,319,697
1949[b]	9,075,903
1950[b]	9,296,051

[a] U. S. Dept. of Agriculture figures.
[b] Figures of Bureau of Census.

(Courtesy of Davison Chemical Corp.)

FIGURE 1. Aerial view of the largest superphosphate plant in the United States, showing docking and storage facilities. Sulfuric acid plants at upper left.

the numerous details affecting the nature of the product. Moreover, the keen competition which has sprung up in the fertilizer industry and the tendency to progress from the old rule-of-thumb practice toward more scientific methods tends to make a thorough understanding of the chemical

principles and changes involved in manufacturing this product extremely important if not essential to commercial success. Phosphate rock from various sources and from different deposits in each phosphate area differs to such an extent that in order to effect the greatest economies in manufacturing superphosphate, more complete chemical analyses than are usually demanded are often necessary, and trial laboratory tests should be made in order to obtain a true index of the proper proportions of sulfuric acid and rock, and the most effective concentration of acid to use. It is a well-known fact that when a new grade or type of phosphate rock is shipped to an acidulating plant a considerable amount of time and material are often consumed in making up large batches or trial mixes before the proper proportions of acid and rock required to give a satisfactory product are determined.

The Mechanics of Superphosphate Manufacture

The manufacture of superphosphate involves the following four very important mechanical or physical operations:

(1) Preparation or grinding of the phosphate rock for acid treatment.
(2) Mixing of the finely ground phosphate with sulfuric acid.
(3) Curing and drying of the acidulated material.
(4) Excavation, milling and bagging of the finished product.

A number of complete or self-contained units for carrying out practically all of these operations with the minimum expenditure of time and labor are now in successful operation in this country, but the majority of superphosphate plants still conduct these various mechanical processes in a number of separate steps.

The apparatus used and the efficiency with which these mechanical operations are conducted have a profound effect on the chemical reactions involved in the manufacture of superphosphate, and hence the improvements in grinding, mixing, handling, milling, and bagging machinery are largely responsible for the economies attained in producing this basic fertilizer ingredient. The writers feel, therefore, that brief descriptions of the various types of machinery and equipment used in the manufacture of this product and a discussion of their functions and merits are essential for a thorough understanding of the process.

Crushing and Grinding Phosphate Rock

The first step in the manufacture of superphosphate is to reduce the phosphate rock to a finely divided condition so that it may be acted upon quickly and completely by sulfuric acid.

Before sending the rock to the pulverizing mills it must first be reduced to a size suitable for the mechanical operation of these mills. This is accom-

plished by passing the rock through a preliminary crusher, where it is broken into pieces less than an inch in diameter. There are several types of mills used for this purpose, such as the Swing Hammer or Sledge Mill, the gyratory or rotary crusher, the jaw and roll crusher.

The hammer or sledge mill is a small machine consisting of a number of flexibly mounted rotating hammers which break up the rock and force it through spaced bars in the bottom of the mill. This type is essentially a high-speed mill and has a large capacity for its size.
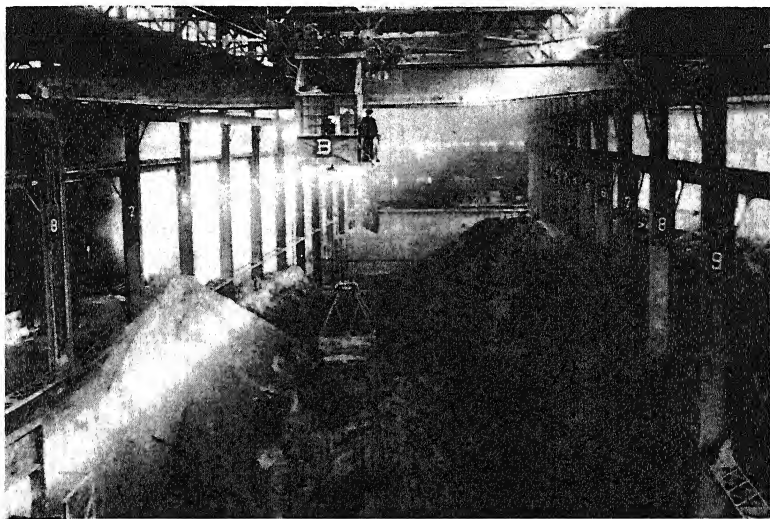
FIGURE 1-a. A modern crane plant for the manufacture of superphosphate, showing handling and storage facilities. The dens are at the far end of the building.

The gyratory or rotary crusher works on the same principle as the household coffee mill and crushes by gradual reduction between the heavy iron cone on the rotating shaft and the chilled iron liner of the mill casing. This is a slow-speed machine, but has a large capacity, and requires little power to operate. The jaw and the roll crusher are seldom used for crushing phosphate rock and will not be discussed in this chapter.

Florida pebble phosphates, however, require little or no preliminary crushing, as the lumps or pebbles are usually small enough to go directly to the pulverizing mills.

Up until about 30 years ago most of the phosphate rock used in the manufacture of superphosphate was ground so that 80 to 90 per cent would pass a 60-mesh screen. Finer grinding was considered uneconomical. With

the improvement in pulverizing equipment and the application of air sepa-
ration, finer grinding was found to be both practicable and economical and
most of the modern plants grind the rock to an average fineness of 80 to
90 per cent through a 100-mesh screen. Whereas, a further decrease in the
size of the rock particles results in a reduction in the acid requirements,
the additional cost of finer grinding may offset the saving in acid thus
effected.

Marshall *et al.*[16] on analyzing freshly prepared samples of triple super-
phosphate made from Montana rock and phosphoric acid (64 per cent
H_3PO_4) found that there was a sharp increase in the solubility of the P_2O_5
as the particle size of the rock was decreased from 80 to 150-mesh, and
Kanowitz[13] reported the following results (Table 2) as representative of the
average quantities of sulfuric acid (51°Bé) per ton of rock of various degrees
of fineness and the relative time required for the reactions to take place.

With fine grinding and thorough mixing of the phosphate rock and sul-

TABLE 2. SULFURIC ACID REQUIREMENTS AND RELATIVE TIME REQUIRED FOR
MAKING SUPERPHOSPHATE FROM ONE TON OF ROCK OF SEVERAL DEGREES OF
FINENESS

Fineness Per cent through 100 Mesh	Sulfuric Acid Pounds of 51°Bé Acid per Ton of Rock	Relative Time For Reaction
95.0	1,739	1.00
90.0	1,842	1.22
85.0	1,946	1.41
80.0	2,058	1.56

furic acid the time necessary to produce a good product has been greatly
reduced. Formerly, the superphosphate manufacturer had to let his product
cure a month or more before shipment. This curing time was necessary
because the coarseness of the phosphate rock treated allowed only the
surface of the larger particles to be acted upon immediately and the acid
permeated the layer of calcium sulfate thus formed around these particles
very slowly. Long standing or curing, however, allowed the acid to per-
meate deeper into the rock particles and a higher yield of available phos-
phoric acid (P_2O_5) was thus obtained.

The extremely fine grinding now so generally adopted gives greater contact
surface for the acid to act on, and allows a more thorough mixing, thus
yielding a product in better mechanical condition, fully matured and ready
for the market within a considerably shorter time. This means a great
saving in that it is not necessary to tie up so much capital in storing the
finished product.

The more concentrated sulfuric acid now used in manufacturing super-
phosphates makes fine grinding even more important because of the limited
solubility of the calcium sulfate in this stronger acid.

The fineness to which the rock is ground is an individual problem which must be governed to a considerable extent by such factors as cost of power, type of rock and the relative prices of the raw materials in the particular locality where the product is manufactured.

The grinding characteristics of the different phosphate rocks vary somewhat, not so much with respect to the phosphate mineral, but chiefly to the impurities, such as flint, sand and clay.

Table 3 shows the relative capacities of a mill grinding rock from different parts of the United States and other world sources. The output of the average Florida rock is taken as unity[13].

Puverizing or fine grinding mills may be broadly grouped into three classes: (1) those which depend on spring tension to hold the rolls against the grinding surface; (2) those which depend upon the centrifugal force

TABLE 3. GRINDING CAPACITY RATIO OF DIFFERENT PHOSPHATE ROCKS

	Ratio
Florida	1
Tennessee	1.2–1.25
Idaho	1.1–1.15
Montana	1.1–1.15
Utah	1.0–1.1
Wyoming	1.0–1.1
Morocco	1.2–1.3
Tunisia	1.2–1.25
Nauru (Pacific Island)	1.3–1.35
Ocean Island	1.3–1.35
Russia (Siberia)	1.0–1.1
Canada (apatite)	1.0–1.1

of steel rolls against a grinding face; and (3) those which depend on the centrifugal force of heavy iron or steel balls rolling over each other within a cylindrical or conical shell. The methods of separating the fine from the coarse material are of two classes, namely, screen and air separation. Air separation has almost completely supplanted the older method of screening the finely ground rock as it is discharged from the mill. Air separation is more positive, cheaper, and gives a more uniform product. The screening of phosphate rock has not only the disadvantage of possible interrupted operation due to the clogging or blinding of the screens, but the wire of such screens eventually wears to such an extent that the screened product becomes coarser. The screens also require constant supervision as they often develop holes, permitting the passage of a considerable percentage of coarse rock which causes trouble when the ground material is subsequently acidulated.

The Kent Maxecon Mill. The Kent Maxecon mill has been popular for many years and is still used in a number of the older fertilizer plants. This pulverizer is constructed and operated on the principle of a free

vertical concave ring, yieldingly supported on three rolls pressing against its inner surface. The ring revolves, so that the material (2 inches, or finer) fed on its inner face is held there by centrifugal force, revolves with the ring, and passes under the rolls which are held up close to the ring by heavy springs. The rolls crush the rock against the ring and discharge it through an opening near the bottom of the mill from where it is carried up by an elevator, and passed through an air separator in closed circuit which removes the fine material and returns the coarser rock to the mill to be reground.

The larger size Maxecon mill will grind from $4\frac{1}{2}$ to 6 tons per hour of Florida pebble phosphate to a fineness of 90 per cent through a 100-mesh screen and requires, for maximum operation, a 75 h-p motor. This mill has been quite satisfactory and many of the superphosphate plants in the South and East are still using it. The main wearing parts are the rolls which must be replaced from time to time.

The Sturtevant Mill and Air Separator. The grinding principle of this mill is much the same as that of the Kent mill except that it is equipped with a door which makes it possible to expose the working parts for repair or adjustment. The mill is operated at a somewhat slower speed than the Kent mill (about 70 rpm for the ring), has approximately the same capacity as a Kent mill of equal size and requires the same power for its operation. This mill is illustrated in Figure 2.

The Sturtevant Whirlwind centrifugal air separator (Figure 3) has proved a very satisfactory machine and a number of the larger fertilizer companies have installed them in connection with their grinding mills. It is operated as follows:

The rock is delivered from a hopper into a chute which discharges it onto a revolving distributing plate operating at high speed. The material is thrown off this plate by centrifugal force in the form of a horizontal spray and the finer material whirled and sucked upward through the large top opening of an inner casing. A secondary or lower fan strongly whirls the upcoming material, centrifugally forcing the coarser sizes away from the opening of the inner casing. The fine material is collected in the outer cone of the separator and the coarse material discharged through an inner cone and returned to the mill for further grinding. A 12-foot diameter separator of this type, capable of turning out from 4 to 6 tons of rock per hour having a fineness of 95 per cent through a 100-mesh screen, requires a 30 to 40 h-p motor for its operation.

Bradley Pulverizer. There are several mills on the market which contain screens as an integral part of the mill itself. The most widely used for grinding phosphate rock is the Bradley three-roll pulverizer (Figures 4 and 5) for which the following advantages are claimed: (1) large output for

low-power consumption; (2) dustless in operation and low upkeep due to the few wearing parts; (3) self-contained unit giving a finished product in
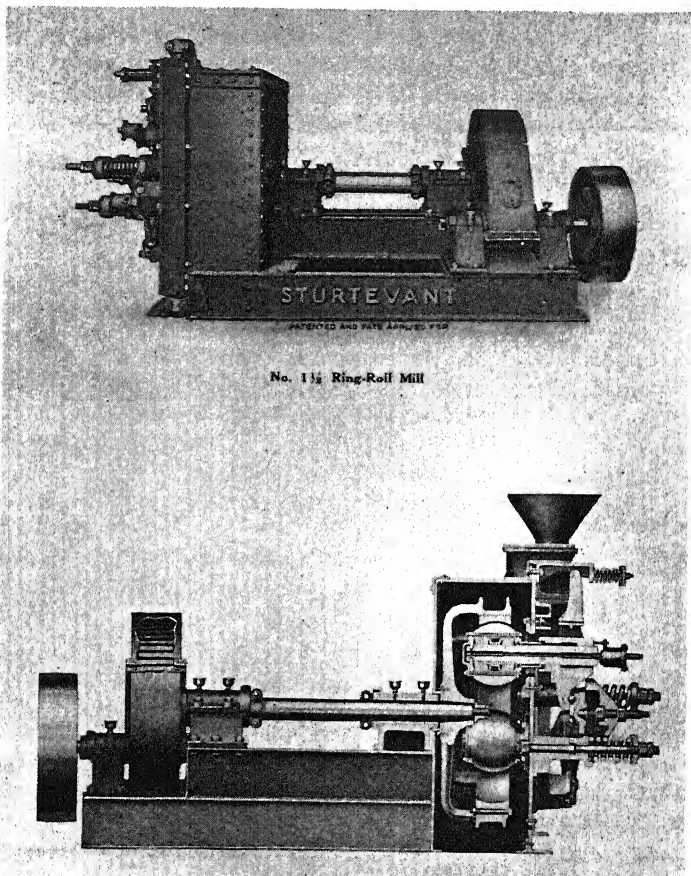
No. 1½ Ring-Roll Mill

(Courtesy of Sturtevant Mill Company)

FIGURE 2. Sturtevant Ring-Roll mill. Upper view shows mill closed. Lower view shows casing cut away and internal structure of machine.

one operation. Although it might appear at first sight that the small screen area in these self-contained mills would materially limit their capacity, an output of 5 to 7 tons of phosphate rock per hour, 70 to 80 per cent of which will pass a 100-mesh screen, is claimed by the manufacturers. This degree of fineness is obtained by using a screen of 12 to 14 mesh in the mill.
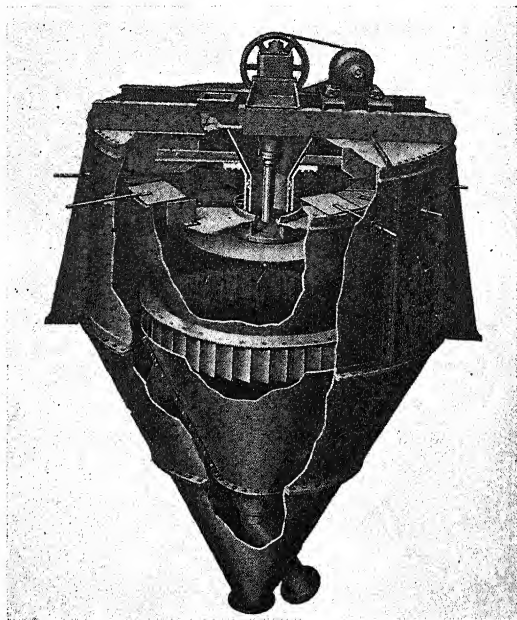
FIGURE 3. Sturtevant Whirlwind centrifugal selector or air separator. Used in lieu of screens for obtaining a very finely pulverized rock.
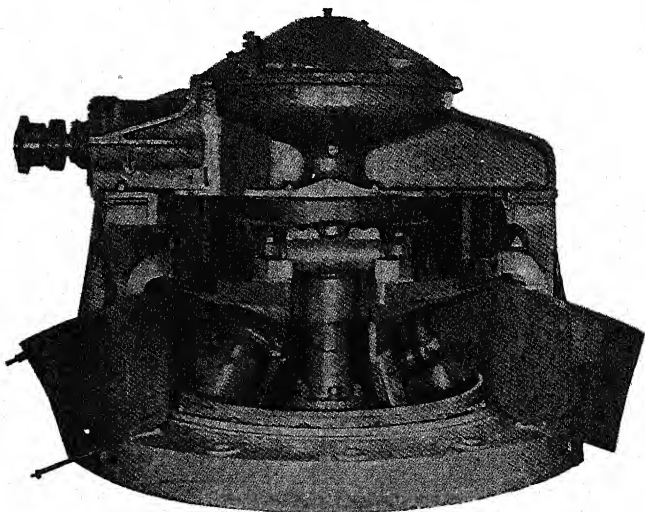
FIGURE 4. Bradley "Hercules" mill with casing removed showing grinding rolls.

One criticism of the self-contained mill is the necessity of closing down when the screen becomes clogged or badly worn.

Those using the Bradley mill do not as a rule grind the phosphate rock to the same degree of fineness that most manufacturers of superphosphate deem desirable.

The Hardinge Mill. The Hardinge conical ball mill is typical of the third type which depends on the crushing action of iron or steel balls against the walls of the rotating steel shell as well as the grinding effect of the balls rolling over each other. This mill is conical in shape and the balls
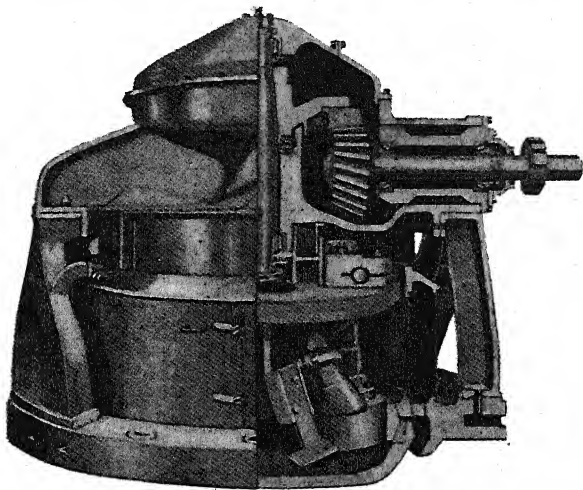
FIGURE 5. Bradley "Hercules" mill. Cut-away view showing driving mechanism.

employed are of hardened steel of various sizes. The large balls are held in the widest part of the cone by centrifugal force and do the coarsest grinding. As the cone narrows to the discharge end, the materials are ground more finely by the smaller size balls. The Hardinge air separating unit consists of a rotating drum, one end of which is connected to the discharge end of the mill and the other end to an exhaust fan which carries the dust-laden air to a cyclone collector.

Because of the lower velocity of the air in the rotating drum the coarser particles of rock are deposited here. The drum is equipped with a helical conveyor and a series of lifters which pick up these coarse particles, as well as the natural discharge from the mill (including both coarse and fine rock), and drop them through the current of air which carries the finer particles to the collector. The coarser material drops into a rotating hopper which

discharges into a return air pipe passing axially through the drum. The air freed from its burden of finely divided rock in the cyclone collector is returned through this pipe at a velocity sufficient to blow these coarse particles back into the mill to be reground. The Hardinge Mill is illustrated in Figure 6.

The Raymond Roller Mill. One of the most popular mills in general use today is the Raymond Roller Mill (Figure 7) which is a completely suspended roller-type of mill for grinding and classifying materials to a
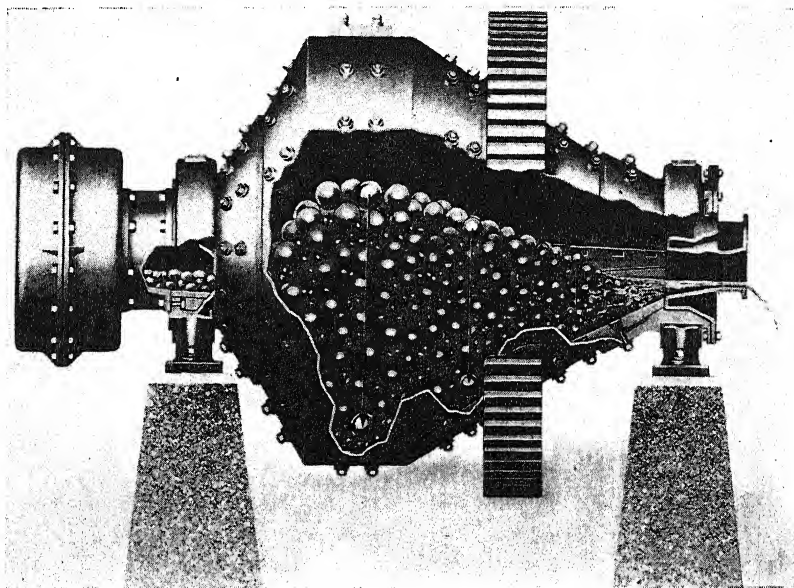
(*Courtesy of the Hardinge Company, Inc.*)
FIGURE 6. The Hardinge conical ball mill.

uniform degree of fineness in an enclosed, dustless system. It is built in two types, known as the low-side and high-side mills. The grinding, conveying and collecting systems are the same in both types. The low-side mill is generally used where a moderate fineness is required or when it is not necessary to frequently change the fineness of the finished product. Changes in the fineness can be made within certain limits by altering the position of adjustable vanes which rotate with the spider carrying the roller forward; also by means of a sleeve which extends down into the separating chamber. This mill is shown in Figure 7.

Generally speaking, for grinding up to a fineness of about 75 to 80 per cent 200-mesh screen, the low-side mill will perform in a very efficient manner.

The high-side mill is equipped with what is called a whizzer separator, an element which, in a general way, resembles a wheel with spokes but without a rim. It rotates in a horizontal plane. All of the ground material has to pass between the spokes, or whizzer blades. Due to the rotation of this
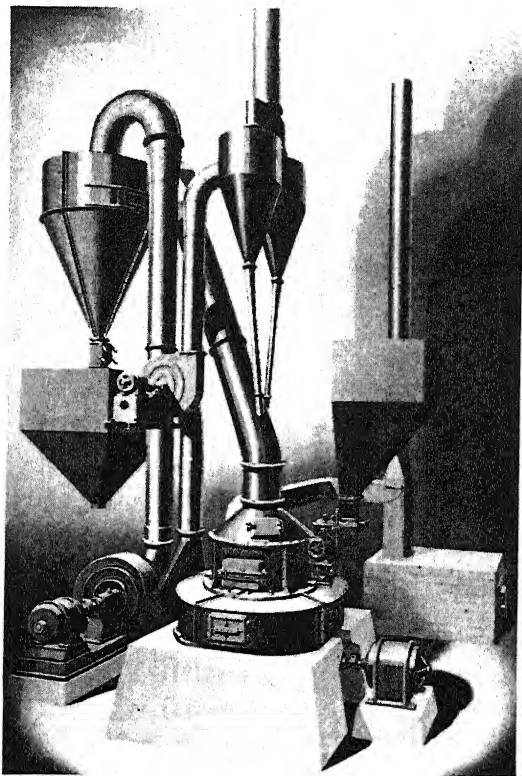
(Courtesy of Raymond Pulvanzer Company)

FIGURE 7. Raymond low-side roller mill equipped with air-drying system.

whizzer element, a centrifugal force is set up which throws the coarse particles to the periphery where they drop back to the grinding surfaces for further grinding. The higher the speed of the whizzer blades the greater is the centrifugal action, so that more particles are returned to the grinding surfaces and the finer particles become the finished product leaving the mill. Since the rpm of the whizzer can be changed through a variable speed device in a few minutes, the fineness of the finished product can be quickly adjusted.

The mill is equipped with an automatic feeder and a feed control so that a maximum output of the mill can be maintained at all times. The control is actuated by the air flow through the mill and if there is a tendency for the mill to overload, a change in the air flow causes the control to decrease the rate of feed to the mill.

No extraneous classifiers or screens are required. In many installations neither elevators nor conveyors for the pulverized material are required, since the circulating air can often discharge the pulverized material through a cyclone collector directly into the bins holding the finished product. Where the rock arrives wet or is exposed to rainy weather the mill can be

TABLE 4. CAPACITIES ON FLORIDA PHOSPHATE ROCK

(Tons per hour)

Fineness		#5048*	#5448†	#6058‡	#6669§	#73612 ¶
50%	200	6.5	8.25	12.0	20.0	28
55%	200	6.0	7.5	10.5	17.0	25
60%	200	5.5	7.0	10.0	15.5	23
65%	200	5.0	6.25	8.75	14.5	22
70%	200	4.75	6.00	8.50	14.0	21
75%	200	4.15	5.25	7.5	12.0	18
80%	200	3.50	4.25	6.0	10.0	15
85%	200	3.25	4.00	5.5	9.0	13
90%	200	2.75	3.25	4.5	8.0	11.5

* #5084, high-side roller mill, 4 rollers.
† #5448, high-side roller mill, 4 rollers.
‡ #6058, super roller mill, 5 rollers.
§ #6669, super roller mill, 6 rollers.
¶ #73612, super roller mill, 6 rollers.

equipped with drying accessories so as to receive hot gases from a furnace which dry the rock while it is being pulverized and conveyed.

Table 4 shows the capacity of five sizes of Raymond mills on Florida rock and the output of the mills at different finenesses on a 200-mesh screen. The corresponding finenesses on other screens are shown in Table 5. These figures may vary somewhat depending on the grade of rock and on the refractory impurities contained, such as silica sand[13].

Table 6 shows the total power requirements for the various sizes of Raymond mills and the necessary auxiliary equipment, including motors for feeder, fan and air separator. Table 7 gives the power consumption in kw-hours per ton of rock when ground to various degrees of fineness in mills of the sizes shown in Table 4.

Table 8 gives the estimated cost of an installation in place. These figures will vary, depending on the locality or country in which the installation is made.

TABLE 5. PERCENTAGES THROUGH VARIOUS SCREENS

−200 mesh	−100 mesh	−80 mesh	−60 mesh	−40 mesh
50	73	80.5	91.5	98.2
55	77	85.0	94.0	99.1
60	82	88.0	96.0	99.8
65	86.5	90.5	97.6	99.92
70	89.5	94.0	98.7	99.96
75	93.0	96.5	99.3	
80	95.0	97.5	99.6	
85	97.0	98.7	99.8	
90	98.6	99.5		
95	99.5	99.8		

TABLE 6. TOTAL POWER REQUIREMENTS

	Mill Size			
	#5448	#6058	#6669	#73612
	h-p	h-p	h-p	h-p
Motors required:				
For mill.........	100	150	250	350
For fan..........	60	75	100	150
For separator....	10	10	10	15
For feeder.......	1	1	1	2–1

TABLE 7. POWER CONSUMPTION (KW HRS PER TON)

Fineness of Rock	Mill Size			
	#5448	#6058	#6669	#73612
50% 200	15.5	14.5	13.75	13.5
61% 200	16.5	15.5	14.75	14.0
75% 200	22.5	21.0	20.00	19.0
80% 200	27.0	25.0	23.00	22.5
90% 200	37.0	35.0	32.00	30.0

TABLE 8. COST OF INSTALLATIONS

	#5448	#6058	#6669
Price of mill...................	$21,000	$27,000	$33,000
Price of motors...............	4,000	5,000	8,000
Foundations and erection......	4,500	5,000	5,500
Miscellaneous costs...........	1,000	1,500	2,000
Total cost in place.........	$30,500	$38,500	$48,500

The figures in Table 9 are based on the operation of a No. 6058 mill, which is considered an average-size mill. The cost of grinding in smaller mills will be somewhat higher and similarly the cost in the larger mills will be less.

The labor involved in the operation of a large mill or several mills is about the same as that required for a small single unit. Therefore, the cost of labor required per ton of product is considerably less for the larger installations.

Depreciation is based on the fact that it might be desirable to write off the mill in ten years, although many of these mills are still in use after 30 years of operation. The power cost is based on a rate of one cent per kw-hour, and the labor cost on a rate of $1.50 per hour. Since these rates

TABLE 9. COST OF OPERATION

	Fineness Through 200 Mesh				
	50%	60%	70%	80%	90%
Depreciation per ton.............	$0.08	$0.10	$0.13	$0.17	$0.22
Interest on investment*.........	.03	.04	.05	.07	.09
Maintenance....................	.06	.08	.10	.13	.16
Power.........................	.15	.16	.18	.25	.35
Labor.........................	.13	.15	.20	.25	.34
Miscellaneous costs.............	.02	.03	.05	.08	.12
Total cost per ton..........	$0.47	$0.56	$0.71	$0.95	$1.28

* Less interest earned on depreciation reserve.

may vary in different localities, the cost figures in Table 9 can be correspondingly changed.

Generally, the additional drying accessories increase the cost of a mill by about 20 to 30 per cent, and where the moisture content of the rock does not exceed 4 to 5 per cent the extra cost of drying may amount to from 15 to 20 cents per ton, the exact amount depending on the type and price of the fuel used.

The Mixing of Phosphate Rock and Sulfuric Acid

Since the manufacture of superphosphate is essentially a chemical process, the thorough commingling of phosphate rock and sulfuric acid is absolutely necessary to obtain a complete reaction and the maximum yield of available P_2O_5. Unless this mixing operation is efficiently performed a considerably larger quantity of sulfuric acid may be used than is actually required to effect the decomposition of the mineral. As a result the product will have a high content of free acid, be in poor mechanical condition and difficult to handle.

In the batch process the general procedure is to charge simultaneously into a mechanical mixer a definite weight of finely ground phosphate rock and a predetermined quantity of sulfuric acid. It is the practice of some operators, however, to charge the rock first and add the acid to the mineral; others prefer to run the acid in first and add the rock to the acid.

In the opinion of the writers the materials should be either introduced simultaneously or the rock added to the acid, otherwise the finely ground rock is apt to ball up and make it difficult to obtain a uniform mixture within the few minutes available before the mass sets.

There are a number of efficient mechanical agitators on the market, but nearly all of those used in the United States are known as the pan mixer which revolves on a vertical axis and has stirring devices which also revolve on their vertical axes within the pan but in the opposite direction to insure efficient agitation. Such mixers are manufactured by the Stedman Foundry and Machine Works. This type of mixer is usually designed to take care of two tons of material per charge and may be briefly described as follows:

A covered cast-iron revolving pan 8 feet in diameter and $2\frac{1}{2}$ feet in depth is carried on ball bearings around its outer circumference. The pan is driven by pinions at a rate of from $4\frac{1}{2}$ to 6 rpm. There is a center discharge opening in the bottom of the pan 18 inches in diameter which is closed by a steel plug fitting into a removable ring. The plug is raised by a lever which simultaneously lowers the scraper into the pan when the material is discharged.

The pan is equipped with two mechanical agitators or stirring devices which consist of heavy cast-iron spiders having 4 arms fitted with steel plows. The tips of these plows are renewable. The stirrers are driven by beveled gears at the rate of 50 to 60 rpm. The pan mixer requires $7\frac{1}{2}$ h-p for its operation.

The cover of the pan is stationary but fits close to the revolving rim and is so constructed that the fumes evolved cannot readily escape. All parts which are subject to wear or corrosion can be readily removed and replaced. A view of such a mixing pan is shown in Figure 8.

In operating this type of mixer, the weighed or measured charges of phosphate rock and sulfuric acid are run into the pan and agitated for a period of from one to three minutes. Before the mass sets up, a lever is pulled which simultaneously raises the center plug and lowers the scraping device, ejecting the material into the den immediately below the mixing pan. The plug closing the opening in the pan is then lowered into place, the scraper raised, and the pan is ready for another charge.

While this type of mixer is operated on the batch principle, the operators become quite skilled in its manipulation and lose so little time that the procedure has almost the advantages of a continuous process. For example,

when the finely ground rock has been introduced into the pan, and the acid is being mixed with this mineral, the operator weighs out a new charge of rock and when the material is being discharged, he starts to weigh the next charge of acid. An experienced operator can mix as high as 40 tons of superphosphate per hour.

The larger superphosphate manufacturers either use two such mixing pans, each of which serves a separate den, or a single mixing pan mounted upon a carriage which can be moved from one den to another.

In recent years continuous mixers have been developed in connection
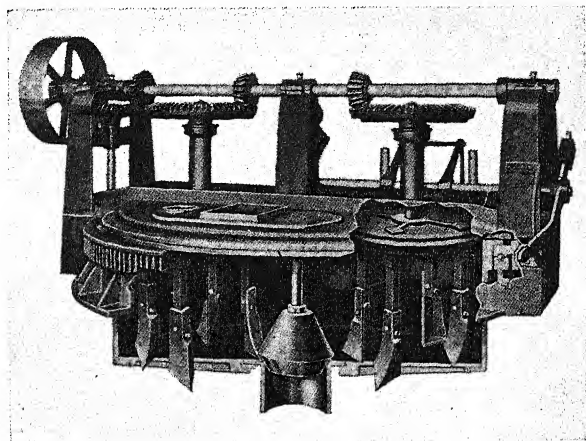
(Courtesy of Stedman's Foundry and Machine Works)

FIGURE 8. Two ton mixing pan for the manufacture of superphosphate.

with the Broadfield and Sackett processes. These are subsequently discussed.

DEVELOPMENT OF THE DEN SYSTEM

In the early years of the industry it was customary to mix phosphate rock and sulfuric acid in vats and then discharge the mixture onto an open pile where it was allowed to age and dry. This open-dump method continued for many years among smaller producers, particularly in the Southeastern states. The method was crude and inefficient, one of its drawbacks being that the heat of reaction was quickly dissipated which retarded the curing and drying of the product. Another objection was that in the vicinity of large towns and farming communities the fluorine fumes evolved during reactions created a health hazard and a potential danger to plant and animal life. This system has been replaced universally by the closed chamber or den method which promotes a speedy reaction between the

rock dust and acid, resulting in the production of a dry, porous type of superphosphate.

The first dens were constructed almost entirely of wood. Then, to prolong their period of usefulness, they were lined with brick. In time this type of construction was generally replaced by rectangular concrete dens and cylindrical silos with greatly enlarged capacities, (100 to 300 tons).

Since many of the superphosphate factories in this country have been installed for some time, the ordinary box-like den constructed of wood or reinforced concrete and having no mechanical device for removing the product is still in use. These box-like dens were originally designed to hold from 20 to 50 tons of material and are so constructed that one side can be raised or removed when it is desired to excavate the material. They usually have a slot 18 inches in width running through the center of the bottom, which is closed when the den is being filled but which is opened to remove the material. Either a pan or belt conveyor is located directly under this slotted opening onto which the product is discharged and conveyed to storage.

The silo-type of den is built like a cylindrical tower of reinforced concrete with a removable top. In excavating such dens a crane equipped with a clam shell bucket is used. The crane-type plant, however, is costly, and the dropping of the bucket onto the column of freshly prepared superphosphate tends to pack the material, necessitating subsequent disintegration. This is being gradually replaced by mechanical dens and excavators.

Mechanical Dens and Excavators

The more modern factories have installed mechanical dens and excavators, the object of which is not only to facilitate the removal of the superphosphate from the reaction chamber but to aerate or partially cure the product.

One of the first mechanical dens in Europe was the Keller and this was followed by the Milch, Wenk, Forbis, Svenska, Beskow, Sturtevant, Maxwell, and others. The Keller was a sort of excavator that could be inserted into an existing den. It consisted of a strong framework with a set of traveling scrapers which pulled the superphosphate to the mouth of the den.

The Milch den comprises a steel cylinder like a boiler shell mounted on wheels which is propelled forward toward a revolving knife by means of screws on each side of the cylinder. The bottom of the den has a series of hinged doors through which the superphosphate drops onto a conveyor as it is cut by the knife. When the mass is completely discharged from the den the screws are reversed, putting the den back to the charging position.

These dens have a capacity of about 30 to 60 tons and are said to be operated very economically.

The Wenk den, which is used extensively in France, is a horizontal cylinder lined with acid-proof bricks into which a cutter travels the reverse manner to the Milch. When the den is full the cutter, which is mounted on a carriage, travels on rails moving in a slot in the bottom of the den. The superphosphate is discharged onto a conveyor belt which runs below the carriage. A Wenk den 6 meters long, 3 meters in diameter holds about 40 tons and requires approximately $2\frac{1}{4}$ hours to excavate.

In both the Wenk and the Milch type dens the cutting knives revolve at about 30 rpm and shave off only a very thin slice. The action reduces the superphosphate to a fine powder, permitting it to dry and cure in a short time.

The Svenska "Den." The Svenska den, developed in Sweden but used to some extent in the United States, comprises a rectangular brick chamber. The front end consists of a door or gate (the full width and height of the den) which is raised and lowered by mechanical means. The discharging device consists of a vertical steel plate or piston which is drawn up close against the movable rear wall when the den is being filled, but which is pushed slowly forward by means of four mechanically operated screws when the den is ready to be discharged. When the den is filled with a mixture of phosphate rock and sulfuric acid it is permitted to react for 15 to 20 minutes, after which it is usually sufficiently set up to be removed.

The gate of the den is then raised and the discharging device or piston pushes the block of superphosphate slowly forward against a mechanical cutting device which crumbles or shaves the material, allowing it to drop into the boot of an elevator. It requires about 3 minutes to empty the den. The elevator carries up the partially disintegrated product and drops it in a continuous stream into chutes which lead to a device called the rasper set into the top of a concrete silo. This rasper consists of a fan-like cutter revolving at high speed on its vertical axis. The material falling through the blades of this cutter is further disintegrated and aerated and drops into the silo below. After remaining in the silo for approximately 12 hours, it is removed and claimed to be ready for shipment. The Svenska system, as far as the discharging and disintegrating equipment is concerned, appears to be quite satisfactory but immediate storing of the disintegrated material in silos for curing has certain disadvantages. These silos contain a long column of material which has not fully reacted. The lower part of the column is hence subjected to heavy pressure which tends to pack the superphosphate and nullifies to some extent the advantages gained in disintegrating the product with the rasping device. A diagram of this den is shown in Figure 9.

The Forbis Den. The Forbis den is a rather expensive piece of equipment and occupies a large amount of space. There are only a few installations in the United States. This den is circular in form, the den proper consisting of an annular concrete ring 8 feet across. The walls of this ring are 8 inches thick and 13 feet high. The total diameter of the circle is 40 feet but the center space is hollow and no material is discharged into it. The den is so constructed that the annular chamber revolves slowly on its vertical axis, but the top remains stationary, being suspended just above the den and sealed to prevent the escape of noxious fumes. The den revolves upon rollers which run upon a circular track and the movement of the den is at the rate of two inches per minute. Upon the top of the den

ACID PHOSPHATE DEN AND UNLOADER
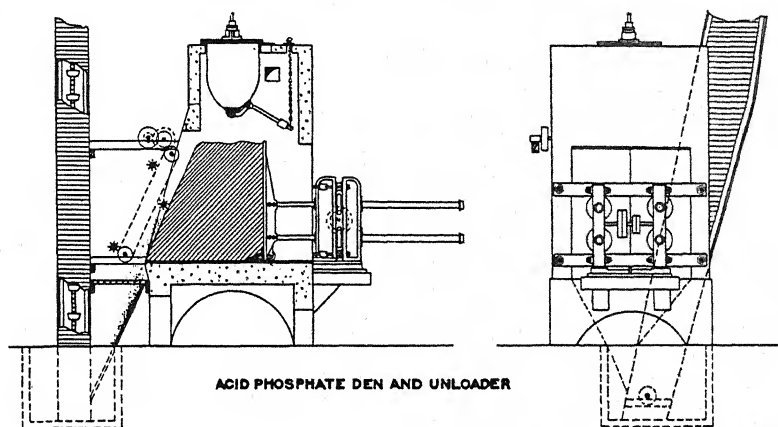
(Courtesy of Armour Fertilizer Company)

FIGURE. 9. Svenska mechanical superphosphate den.

is mounted the mixer which is of the pan-type previously described. The weighing devices for acid and rock are suitably mounted above this mixer Two flues are provided, one for removing the gaseous fumes from the mixer and another which takes care of the gases evolved from the den.

A combined cutting device and excavator is also mounted on this platform or cover and extends down into the den, shaving off thin sections of the porous mass, elevating it, and dumping it into cars for removal to the storage pile. This excavator is so spaced from the mixer that it cuts and removes only the superphosphate which has been in the den for the longest period of time, the speed of the apparatus being so regulated that the material excavated is at least 8 hours old. The installation at one of the plants in a southern state produces 270 tons in 9 hours or at the rate of 30 tons per hour.

Whereas the Forbis den is very large and costly, the power consumption

is relatively low. A 5 h-p motor is required to operate the den or a total of 50 h-p for the den, conveyor, and elevator.

The Sturtevant Den. The mechanical den designed by the Sturtevant Company for the rapid manufacture and curing of superphosphate is favored by a large number of manufacturers in the United States. While it lacks the advantage of being a continuous process such as the Broadfield type, its simplicity and upkeep is such that it has much to recommend it. It consists of a rectangular chamber having a concrete base ánd wooden side walls which are hinged at the top to allow them to swing outwardly when the den is being excavated. When the den is being filled, however, these side walls are fastened at the base by wedges and held in place until the block of superphosphate sets sufficiently to stand alone. The den may be constructed so that the concrete base moves forward into the cutting device or the base may be rigid so the cutting device moves into the block of superphosphate after the side walls of the den are swung outward preparatory to excavating the product.

The excavator, which is directly in front of the den, consists of a circular steel framework bolted to a vertical shaft and carrying a system of aerating fans and a series of cutting knives arranged in staggered relation to one another. The front end or door of the den is suspended by counter-weighted chains from a rigid superstructure which also carries the weighing devices and the mixer for the acid and the rock.

In filling this den the front door is lowered and the sides fastened at the bottom by wedges to prevent their swinging outward. The den is then filled in the usual manner with weighed charges of acid and phosphate rock which have been thoroughly stirred, and the material is allowed to set for 20 minutes. The front door is then raised, the wedges removed from the lower end of the side walls allowing them to swing free, and the block of superphosphate either pushed forward into the cutter or the cutter moved slowly toward the superphosphate according to the type of den best suited to space conditions in the factory. The excavator cuts its way into the mass shaving off thin sections, which are at the same time aerated by the fan-like blades carried on the excavator. The disintegrated phosphate falls upon a conveyor at the side of the apparatus or into the boot of an elevator from whence it is discharged into cars which convey it to storage. The Sturtevant den and excavator are illustrated in Figure 10.

THE OBERPHOS PROCESS,

This process was a radical departure from the conventional den method. The primary aim was to improve particle size, dryness and hygroscopicity of the superphosphate, and it was successful in producing a granular free-flowing, non-setting product of superior handling and mixing qualities.

The process was developed under the sponsorship of G. Ober and Sons Co., in Baltimore, Maryland, in the late 1920's[27].

The process may be briefly described as follows: Weighed charges of acid and rock dust are simultaneously forced into an evacuated rotating autoclave. The valves at both ends of the autoclave are immediately closed and steam introduced directly into the charge to raise the temperature of the mass to 300°F and the pressure to 90 psi.
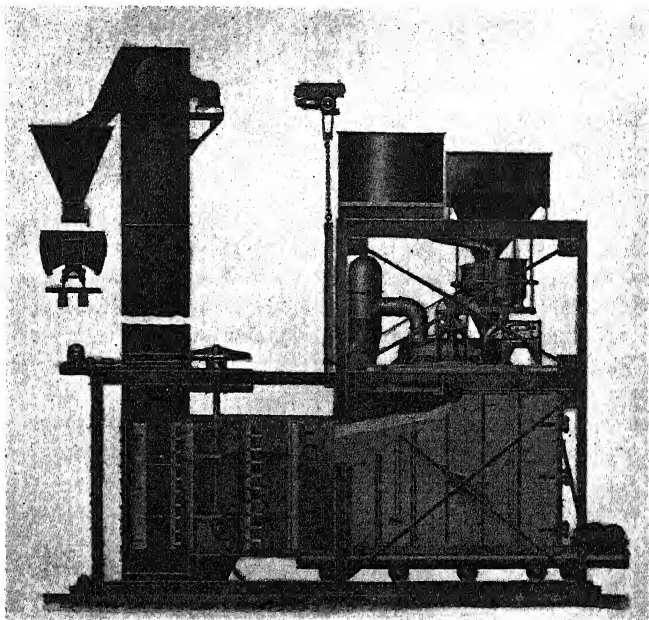
(Courtesy of Sturtevant Mill Company)
FIGURE 10. Sturtevant mechanical den and excavator.

The mixture of acid and rock dust is digested under pressure for a period of 20 minutes. The pressure is then released and the material dried under a vacuum of 28 inches for 30 minutes. The machine is stopped while the manhole at the center of the autoclave is opened, the autoclave again started and the product automatically discharged in the form of small balls or pellets. The main objection to the Oberphos process is the heavy capital investment required for a limited output. A plant with a single autoclave of the size described produces about $5\frac{1}{2}$ tons of superphosphate per hour, whereas an ordinary plant equipped with a two-ton pan mixer and Sturtevant den can produce from 30 to 40 tons in the same length of

time. The Davison Chemical Company of Baltimore, Maryland, acquired the properties of G. Ober and Sons, Co., and is now producing granular superphosphate by a modification of the Oberphos process, described subsequently in this chapter.

Continuous Superphosphate Processes

The advantages of continuous processes for manufacturing superphosphate were long recognized, but have only been developed on a commercial scale within the past twenty years. In Europe such systems are represented by the Maxwell, Nordengren and the Moritz-Standaert processes, the merits of which are discussed by Parrish and Ogelive[22]. In the United States continuous systems have been developed known as the Broadfield and Sackett processes.

The Maxwell Process

In the Maxwell process the carefully proportioned charges of rock dust and acid flow continuously into a trough-like mixer and the resultant slurry discharges into an unique type of den which resembles a large upright automobile tire (19' external diameter and 5'6" in cross section) built of cast iron and slowly revolved at the rate of 1 revolution every four hours.

The slurry of rock and acid enters the lower part of the trough formed by this tire and as the superphosphate sets it is carried upward. When it reaches the uppermost position, it is excavated by means of a revolving cutter, drops into a chute and hence onto a conveyor which takes it to storage for final curing. A suitable duct connected with an exhaust fan draws off the fumes. The capacity of such a den is rather low (about 5 tons per hour) and the power requirements per ton of product appear rather high.

The Nordengren Process

This is a continuous-type process developed in Sweden. The inventor claims it has a greater uniformity of operation and lower power consumption than any other process. It is unique in that the mixing is done in two stages and in two separate mixers. All of the acid of 60°Bé needed for the conversion of a predetermined amount of phosphate rock is introduced into the first of the two mixers, but only a portion of the rock. Apparently the purpose of the excess acid in the first stage is to maintain the mixture in the form of a slurry so as to convert the maximum amount of the phosphate into phosphoric acid. After the sludge is thoroughly mixed it is run into the second mixer where the remainder of the phosphate rock is added. The inventor stresses the importance of weighing the rock dust accurately

in order to obtain a product of uniform quality. The mixture then flows from the second mixer into a rectangular-shaped den having fixed walls, back and sides but the floor of which consists of a conveyor constructed of steel plates. A horizontal scraping device at the discharge end of the conveyor is used to shave off the block of superphosphate. A Nordengren installation is compact; a 40-ton per hour unit will occupy a floor space of 18 by 6 meters.

The Moritz-Standaert Process

This continuous-type process closely resembles the Broadfield method, except in its den construction. The product it turns out contains, like the Broadfield, only 10 to 11 per cent moisture. A typical unit has a capacity varying from 12 to 25 tons per hour and a higher strength acid than ordinarily used is required in its operation for a desirable dry-end product. The mixer consists of a "U" shaped trough provided with stirring paddles which rotate in opposite directions. The rock dust is measured by volume and enters one end of the mixer in continuous flow, while the acid is fed continuously through a graduated tube. As the paddles mix and knead the mass they slowly move it toward the outflow and into the den below.

The den (lined with concrete) is cylindrical and revolves around a central axis. A fixed platform tops the den and supports the mixing and cutting devices. A cast-iron plate is attached to the platform to divide the den between the mixing and excavating device and its presence serves to prevent freshly mixed material from running back to the cutter which lies behind the mixer.

The superphosphate moves around in the annular space in the container formed between the concrete wall and the cast-iron central mandrel, toward the slicer. The superphosphate hardens during the slow rotation of the den and forms a ring which comes in regular contact with the rotating cutter. The shavings drop onto a conveyor in fine, uniform sized particles.

A powerful suction fan carries off the gas and steam evolved by the chemical reaction. This fan, which creates a draft of about 1300 cubic meters of air at 110°F per ton of superphosphate produced, helps greatly to produce a superphosphate of low-moisture content.

It is claimed one man can look after this process and still have time to supervise the grinding mills. It is designed so all the controls are centralized. Power consumption is small; a 20-tons-per-hour operation consumes a total of 1.0 kw-hour per ton of superphosphate made. The Moritz den is shown in Figure 11.

Broadfield Process

The Broadfield self-contained unit is an American invention for the manufacture of superphosphate by a continuous process. The equipment

required may be briefly described as follows:

A bucket elevator carries the finely ground phosphate rock up to a hopper which is kept full at all times while the plant is in operation. Any excess of rock dust is returned to the boot of the elevator. From this rock hopper the finely ground material drops into the pockets of a rotating
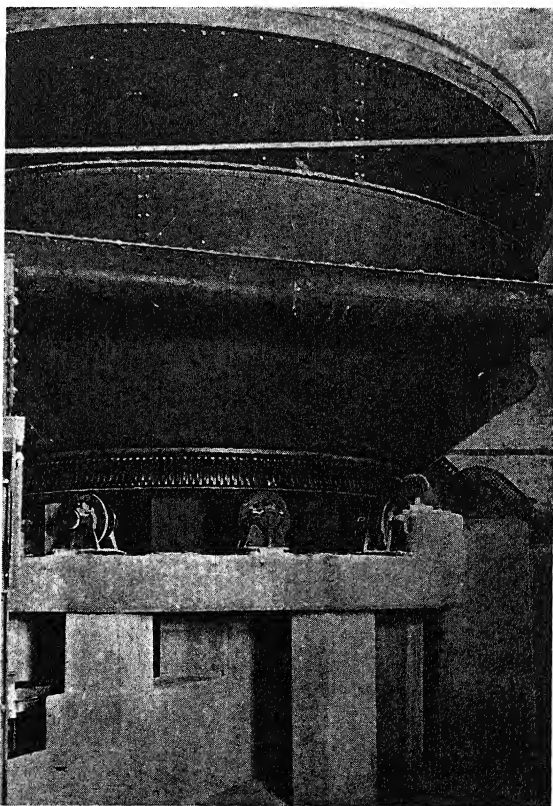
FIGURE 11. Moritz den for the continuous manufacture of superphosphate.

feeding device; the rate of feed is controlled by the speed of the rotating device and also by the size of the pockets.

The feed for the sulfuric acid consists of a tank in which a constant head is maintained by pumping acid to this tank and returning the overflow to the supply tank. The rate of flow from this feeder is regulated by the size of the orifice in the end of the pipe leading to the mixer. The size of this orifice is adjusted in turn by cementing glass tubes of different bores into the end of this pipe. One of the features of the latest design

feeder is its ability to feed at a uniform rate regardless of the wear of the mechanical parts.

The acid and rock dust are fed simultaneously and continuously into a mixing device consisting of a cast-steel trough, 14 feet in length, 2 feet deep, and 2 feet inside diameter. Through the entire length of this mixer is a horizontal shaft rotated at a speed of 170 rpm; fitted around this shaft is a series of mixing blades so designed that some of them advance the slurry of rock and acid toward the far end of the trough, while others tend to hold the material 'back. There is a hood over the mixer with a flue leading to a series of towers fitted with water sprays through which the evolved gases are drawn by means of an exhaust fan.

The thoroughly mixed material is discharged from the mixer into a mechanical den which consists of a slow-moving conveyor (3 feet wide and 30 feet long) originally composed of wooden slats, but now replaced by steel slats. The side walls of the den are also made up of slats and these walls move at the same speed as the conveyor so that the partly set up superphosphate does not drag along these walls. The slats of the conveyor or floor extend beyond the walls of the den and have blocks fastened to their ends to serve as guides for the den walls. A suitable top fitted with a flue which leads to the absorption towers serves to keep the fumes evolved in the den from escaping into the plant. The den or conveyor moves at the rate of 4 feet per minute so the material remains in this reaction chamber for about $1\frac{1}{4}$ hours.

At the far end of the den the material discharges into a rotating cutting device fitted with staggered blades which shave off the superphosphate and drop it into the boot of an elevator. The elevator in turn discharges the disintegrated superphosphate into side dump cars which carry it to storage. An assembly plan of the Broadfield continuous den is shown in Figure 12, and views of the mixer and discharge end of the den are shown in Figures 13 and 14.

Sackett Super-Flow Process

This continuous method of manufacturing superphosphate is a fairly recent development. Its most striking feature is the manner in which the initial mixing of the phosphate rock and sulfuric acid is effected. The process and the equipment employed may be briefly described as follows:

The finely ground phosphate rock is discharged from a silo-type storage bin into a screw conveyor and hence into a bucket elevator. The latter delivers the ground rock to a continuous weighing machine through feeders so designed that there will be no uneven flow or sudden surges of the pulverized rock which interfere with accurate weighing. The scales are set to supply continuously 25 tons of rock per hour and are sensitive to within
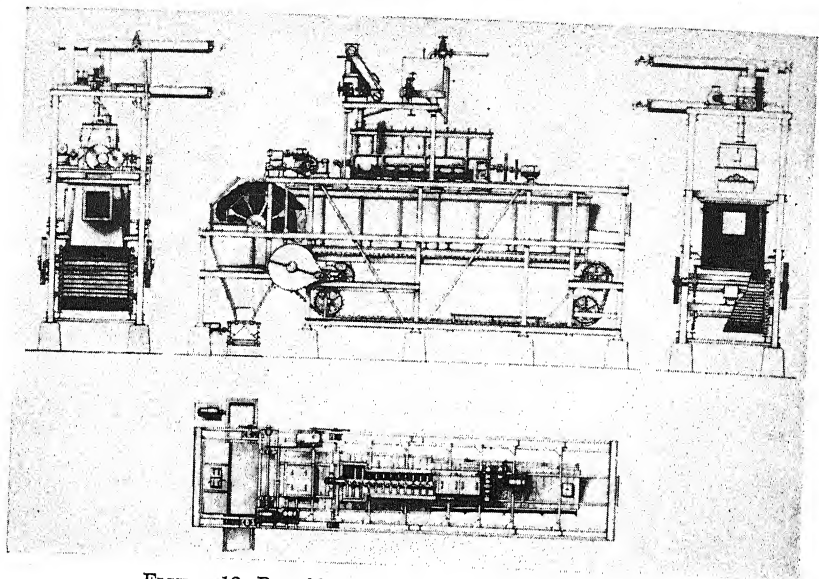
FIGURE 12. Broadfield continuous superphosphate den.
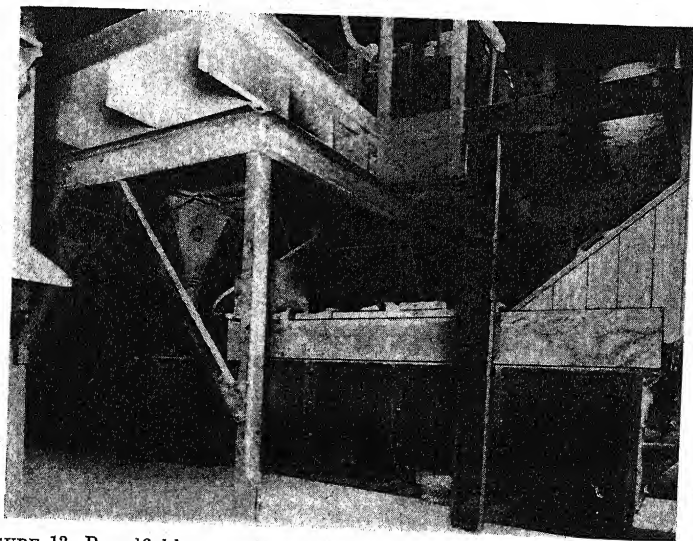
FIGURE 13. Broadfield process for producing superphosphate. Continuous mixer with control platform above.

1 per cent of the prescribed weight. An automatic device shuts off both the rock and acid feeders if the plant is not receiving its proper quota of either rock or acid.

After being weighed the finely ground rock is fed into a bucket elevator which discharges into the top side of a horizontal steel duct through which
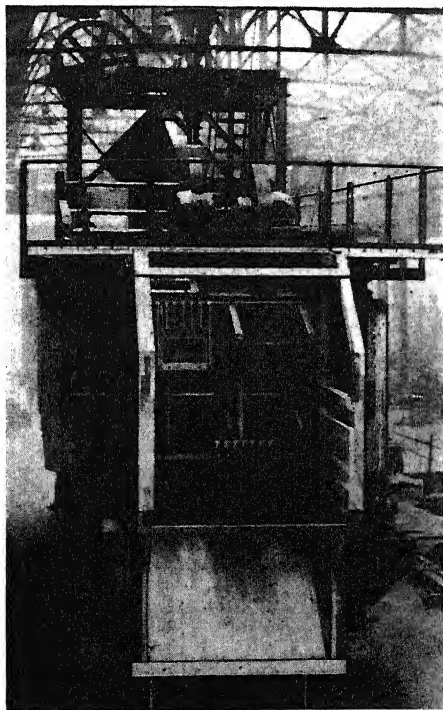
FIGURE 14. Broadfield process for producing superphosphate. Discharge end of continuous den showing cutters.

air is forced. This air current carries the rock dust forward and introduces it tangentially into the upper side of a cylindrical rubber-lined acidulating tower.

The sulfuric acid (having a concentration of 56°Bé) is pumped to this acidulating tower through a stainless steel atomizing nozzle set in the center of the top of this tower; the quantity of acid and rate of delivery are carefully controlled by a flowmeter. The atomized acid forms a spray cone having a 60° included angle and this spray penetrates the cyclonic
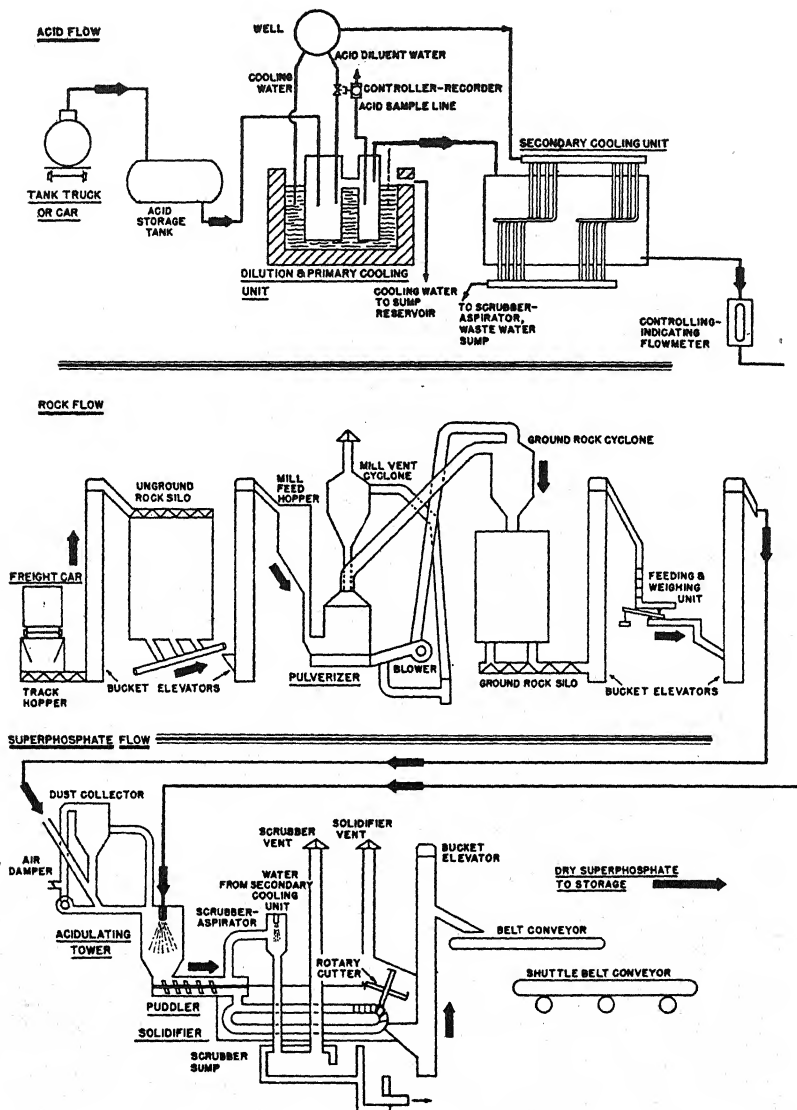
(Courtesy of A. J. Sackett & Sons Company Baltimore, Maryland)

FIGURE 15. Plant layout and flow sheet of the Sackett "Super Flow" Process for the continuous manufacture of superphosphate.

turbulent cloud of rock dust facilitating thorough and rapid mixing of the two ingredients.

The resultant superphosphate in the form of a thin slurry drops to the bottom of the reaction chamber and is discharged continuously into a supplementary mixer or puddler consisting of a rubber-lined trough equipped with a horizontal central shaft to which are bolted propelling flights for kneading the material and conveying the rapidly thickening product to the den. An aspirator serves to draw off the gaseous fluorine compounds evolved in this mixer through a suitable duct.

The den or so-called solidifier into which this second mixer discharges consists of a completely housed slow-moving channel-like conveyor made up of U-shaped plates. A suitable vent is provided for the escape of any residual fluorine gases. At the far end of this mechanical den or conveyor a rotary helical cutter serves to disintegrate the superphosphate. The disintegrated product, is elevated, fed upon a belt conveyor and distributed on a storage pile. The product has a hard porous grain structure that minimizes subsequent set and facilitates handling and distribution.

The inventors claim that this process offers substantial economies in both labor and power consumption. They state that three men can operate a 45 ton per hour plant with a power consumption of only 1.12 kw-hour per ton of finished product as against a crew of 10 to 12 men and a power consumption of 1.75 kw-hours for a plant of equal capacity employing the batch process.

A flow sheet of the Sackett process is given in Figure 15. The reader is referred to an article by Demmerle and Sackett[2] for a more detailed description of the various steps involved.

CURING, DRYING AND GRANULATION OF SUPERPHOSPHATE

Superphosphate excavated from the den within 1 to 24 hours has a temperature well above the boiling point of water (110 to 120°C) but the product has not reached equilibrium and still contains appreciable percentages of free acid and some residual or unconverted phosphate rock. In order to reduce the free acid to a minimum and convert the maximum amount of P_2O_5 into an available form, the product is conveyed to huge storage piles for final curing, which requires from 2 to 4 weeks depending on the nature and proportions of the raw materials used and the manufacturing conditions.

Whereas freshly prepared den superphosphate quickly attains an initial set, there is still the tendency to form crystallized monocalcium phosphate and limited quantities of crystallized calcium sulphate or gypsum which cause the product to again set in the storage pile.

In order to minimize this set and prevent the product from becoming too hard during the final curing period, it is customary to aerate the product as soon as the superphosphate is removed from the den. This is done by dropping the material from a considerable height either by means of dump cars located on an elevated track near the top of the storage building or by dropping it from a crane bucket. In falling from a height ranging from 10 to 50 feet the material not only breaks up, but spreads out in relatively thin layers which facilitates the escape of water vapor and tends to cool the freshly prepared product.

The storage buildings are usually so designed that the superphosphate which has been cured for the longest period of time is the most easily accessible for shipment; for instance, in one of the more successfully operated plants in Baltimore, the storage shed, which is of the "A Frame" type, is filled by means of side dump cars holding approximately 5 tons product. These cars are loaded from hoppers into which the elevators serving these dens discharge the freshly prepared superphosphate. The cars are then run out upon elevated tracks (which extend the full length of the storage building) and discharge the material on the storage piles. To facilitate shipment of the product, this company stores the superphosphate in two piles. A lane or free passage is maintained between the piles and when the superphosphate plant is operating, the material excavated from the den is dumped close to the free lane or passage; as this space becomes filled, the cars discharge their loads further and further back toward one end of the building until nearly half of the storage building is completely filled.

A similar pile of superphosphate is then built up on the other side of the free lane or passage until the other half of the storage shed is filled. In this way the superphosphate which borders the free lane or passage has been aged to a greater extent than that further back, and when the time comes for shipping the product, this cured material is removed first.

In crane-operated plants, however, where grab-buckets can be moved the full length of the storage shed, it makes little difference where the freshly prepared superphosphate is stored, provided care is taken not to mix it with the aged product.

The excavation of the cured product preparatory to shipping is accomplished in several ways. One method consists in using small, easily operated steam shovels which cut into the pile and discharge their load into gasoline or electrically operated cars on the ground level of the storage shed. These small cars dump their loads upon a 3-inch steel grating which covers the pit of an elevator. Any large lumps are broken up by pick and shovel and passed through the steel grating along with the fine material. The elevator then carries the partially disintegrated product to the upper part of the

building where it is discharged into a hopper which feeds a disintegrator either of the hammermill or cage mill type. Such mills discharge the disintegrated superphosphate upon inclined screens so that the final product contains no material coarser than 6 mesh. All material not passing such screens is returned to the mill to be reground.

In crane-operated plants, a clam-shell bucket scoops up the material from the storage pile and drops it into a hopper covered by a steel grating similar to that used over the boot of the elevator in the type of plant just described. From this hopper the product feeds to the mill or disintegrator and finally to the screens. The screened product is then elevated and discharged into cars which carry it over a trestle to the loading hoppers. From these hoppers the product is discharged through spouts directly into the holds of vessels or into boxcars located under the trestle.

At some plants the milled or disintegrated superphosphate is discharged from the hoppers upon belt conveyors which lead to the loading platform. Here a portable loader piles the material toward either end of the boxcar. Where superphosphate is to be used directly upon the soil and not mixed with other fertilizer ingredients, the storage hopper for the disintegrated product surmounts a bagging machine mounted on automatic scales and the product is discharged directly into bags which are weighed, sewed and then loaded into cars or into the holds of vessels.

While burlap bags treated with paraffin are the most widely used containers for superphosphate, in recent years, water-proofed paper bags have come more and more into favor, and bagging machines for handling this latter type of container have been devised which fill, weigh, and seal the bag with a minimum amount of handling. Superphosphate shipped in bulk is sold on a run-of-pile basis, which means that the purchaser pays for the available P_2O_5 in the product and does not specify a given analysis. Most of the run-of-pile material contains from 18 to 20 per cent of available P_2O_5. Superphosphate shipped in bags, however, for direct application to the field is usually sold on the basis of a guaranteed analysis. This analysis ordinarily runs from 16 to 18 per cent of available P_2O_5. To produce such material, the run-of-pile superphosphate may be diluted with some inert material or filler to give the desired composition. The fillers employed for this purpose are silica sand and dolomitic limestone. The latter material has the advantage of neutralizing free acidity without reverting the available P_2O_5 to an insoluble condition. Free or hydrated lime as well as limestone (consisting chiefly of calcium carbonate) must be used very sparingly if at all, as these materials tend to convert available P_2O_5 into an insoluble condition.

Well cured superphosphate, particularly that made by mixing finely ground phosphate rock with relatively concentrated sulfuric acid (54 to

$56°$Bé) does not ordinarily require artificial drying. If however, it is desired to raise the grade of the product by driving off the free moisture and even some of the water of crystallization, this can be done without injuring the final product provided care is taken not to heat the superphosphate too high.

As discussed in the latter part of this chapter, the bulk of the calcium sulfate in superphosphate is present as anhydrite and only minor quantities are in the form of either gypsum ($CaSO_4 \cdot 2H_2O$) or hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$). Therefore, heating the product has little or no effect on the calcium sulfate other than driving off any free moisture contained therein.

Monocalcium phosphate however is present largely in crystalline form ($CaH_4(PO_4) \cdot H_2O$) and this compound loses its water of crystallization when heated to $120°C$. Moreover, at a temperature of $150°C$ anhydrous monocalcium phosphate loses some of its water of constitution forming acid calcium pyrophosphate. Finally, on heating to a higher temperature the acid calcium pyrophosphate decomposes giving up a further quantity of water and is converted into calcium metaphosphate. The following equations represent these three successive decomposition steps:

$$CaH_4(PO_4)_2 \cdot H_2O + Heat \rightarrow CaH_4(PO_4)_2 + H_2O \qquad (1)$$

$$CaH_4(PO_4)_2 + Heat \rightarrow CaH_2P_2O_7 + H_2O \qquad (2)$$

$$CaH_2P_2O_7 + Heat \rightarrow Ca(PO_3)_2 + H_2O \qquad (3)$$
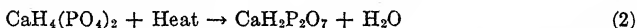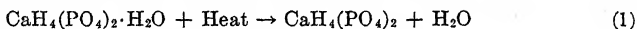
The two derivatives of monocalcium phosphate shown in equations (2) and (3) are only sparingly soluble and in general are not as favorably regarded for fertilizer purposes as monocalcium phosphate.

Only minor quantities of crystalline dicalcium phosphate usually occur in superphosphate but this compound also loses its water of crystallization at elevated temperatures. Moreover, further heating of the anhydrous salt will cause its decomposition into calcium pyrophosphate, a highly insoluble compound having little or no fertilizer value. These successive reactions are represented as follows:

$$CaHPO_4 \cdot 2H_2O + Heat \rightarrow CaHPO_4 + 2H_2O$$

$$2CaHPO_4 + Heat \rightarrow Ca_2P_2O_7 + H_2O$$
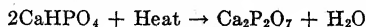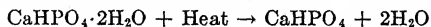
The hydrated phosphates or sulfates of iron and aluminum in superphosphate also lose water at elevated temperatures and no doubt affect the availability of the P_2O_5 in the final product, but the final reactions involved are not entirely clear because of the complex nature of these compounds.

It appears to be safe to dry well cured superphosphate at a temperature not exceeding $120°C$, but freshly made or green superphosphate should

not be heated to a point where all of the free moisture is driven off. By eliminating the liquid phase further reaction is arrested and the maximum possible solubility of the P_2O_5 in the superphosphate will not be effected even after long curing in the storage pile.

Granular Superphosphate

During recent years much attention has been given to the preparation of granulated superphosphate[6, 15]. The advantages claimed for this material are as follows:

(1) Because of its granular nature and fewer points of contact it has less tendency to set when stored in large piles or mixed with other fertilizer ingredients.

(2) It is a more highly concentrated product with respect to P_2O_5 than ordinary superphosphate due to its lower moisture content.

(3) It is easily handled and can be more uniformly distributed in the field.

(4) It releases available P_2O_5 to the soil solution at a rate commensurate with crop needs and consequently there is less fixation of the soluble phosphate by the bases in the soil.

There is ample proof that granulated superphosphate meets the first three conditions outlined above and experiments both in the greenhouse and in the field have been and are still being conducted to compare the relative merits of this granular material with the fluffy, more finely divided product obtained directly in ordinary dens. These tests have not been altogether conclusive, but there is some evidence that granulation improves the utilization of the P_2O_5 by crops grown on soils of high phosphorus fixing power[20].

Whereas the Oberphos process previously described was designed to produce a granular product directly, this process has the disadvantage of a rather limited production unless a large and costly plant is installed.

The following processes of granulation are given by Procter[23]:

(1) Pressure and extrusion methods.

(2) Self-aggregation of particles by moistening, tumbling, and rotary drying.

(3) Flaking or shredding solid or semi-solid materials, followed, if necessary, by drying and screening.

(4) Dispersing and cooling a melt.

(5) Building up granules by layering and drying successive coatings on pellets which are mixed in great volume into a suspension of the same material in saturated solution. This is known in the United States as seeding.

Of the above processes, (2) is the most generally used. This represents

a simple principle and is applied at a number of plants in Great Britain and at the Curtis Bay works of The Davison Chemical Corporation in the United States. Process (5), developed by the Dorr Company, is being used at the Trail, B. C. (Canada), plant of the Consolidated Mining and Smelting Company, and at the Mathieson Chemical Company plant in Texas.

The Davison Process[4]. This process has been described in detail by Mackall and Shoeld[15]. It is conducted in two broad steps: In the first step, the green den superphosphate is conditioned and granulated by feeding it into a slightly inclined rotary steel drum (8 x 40 feet). As the superphosphate enters this drum it is sprayed with sufficient water, (not over 10 per cent of the weight of the superphosphate), to dampen the material sufficiently to cause the formation of globules or pellets as the drum revolves.

From the far end of the drum or granulator, the product is discharged into the cool end of a rotary, direct-fired drier of the same size and construction as the drum, except that it contains flights to facilitate the drying operation. The product is finally discharged from the hot end of the drier in the form of hard, dry pebble-like particles.

Since the size of the granular particles may vary considerably, the product is run through a hammermill and then over double-decked vibrating screens. All particles coarser than 6-mesh are reground, while the very fine material (−60 mesh) is returned to the system and again granulated.

This process of granulation is adapted to produce either straight superphosphate or a complete fertilizer mixture. In granulating superphosphate it has been found that the warm and moist product direct from the den is easier to pelletize than the cured material, but as indicated previously, it is highly important in granulating uncured superphosphate that some free moisture remain in the product. Otherwise, further chemical reactions will be prevented or greatly delayed and the full conversion of the insoluble P_2O_5 into an available form will probably never be attained.

THE CHEMISTRY OF SUPERPHOSPHATE MANUFACTURE

The four principal objectives sought in the manufacture of superphosphate are:

(1) To obtain a product containing the maximum percentage of P_2O_5 soluble in the conventional medium (neutral ammonium citrate) designated by the American Association of Official Agricultural Chemists as a measure of the availability of phosphates.

(2) To eliminate the maximum amount of moisture whereby the percentage of P_2O_5 is not only increased but the mechanical condition of the product improved.

(3) To bring about the desired chemical reactions and the drying and conditioning of the product so it may be shipped in the least possible time.

(4) To employ the smallest possible amount of sulfuric acid to obtain the results enumerated above.

By using high-grade phosphate rock and the most up-to-date mechanical equipment the first three objectives have been satisfactorily met, but though manufacturers have tried to reduce the amount of sulfuric acid necessary to change the phosphate into an available form very little success has been attained.

If phosphate rock were practically pure phosphate of lime its treatment with sulfuric acid and the preparation of a uniform product of proper chemical composition and in good mechanical condition would offer little difficulty. Even the highest grade phosphate rock, however, is not pure tricalcium phosphate, hence the sulfuric acid added not only acts upon the phosphate of lime but upon the calcium fluoride tied up in the apatite molecule, and directly or indirectly upon such impurities as organic matter, iron and aluminum compounds and carbonates of lime and magnesium, all of which consume a certain amount of acid and form products affecting the chemical and physical properties of the superphosphate. Therefore, the main reactions involved between sulfuric acid and phosphate of lime as well as the minor reactions brought about between this acid and the impurities contained in phosphate rock are described.

It is generally agreed that the main ingredient of most high-grade phosphate rock is fluorapatite $(3Ca_3(PO_4)_2 \cdot CaF_2)$, a compound in which the fluorine is a constituent part of the phosphate molecule. From a practical standpoint, however, the phosphoric acid (P_2O_5) may be considered as combined with lime (CaO) as tricalcium phosphate $(Ca_3(PO_4)_2)$ and the fluorine present in the form of calcium fluoride (CaF_2) as a separate compound or acid consuming impurity.

Tricalcium Phosphate

Tricalcium phosphate treated with sulfuric acid is converted into a mixture of calcium sulfate and hydrated monocalcium phosphate. These two compounds are the chief constituents of ordinary superphosphate. This main reaction may be quantitatively represented as follows:

$$Ca_3(PO_4)_2 \quad + \quad 2H_2SO_4 \quad + \quad H_2O \quad \rightarrow$$

Tricalcium   *Sulfuric Acid*   *Water*
Phosphate   (1 molecule, wt. 18)
(1 molecule, wt. 310)   (2 molecules, wt. 196)

$$2CaSO_4 \quad + \quad CaH_4(PO_4)_2 \cdot H_2O$$

Calcium   *Monocalcic*
Sulfate   *Phosphate*
(2 molecules, wt. 272)   (1 molecule, wt. 252)
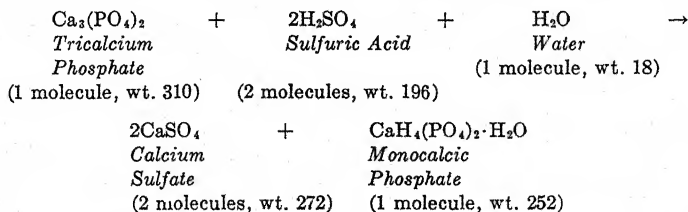
The above equation means that in order to change completely 310 parts of pure tricalcium phosphate into hydrated (crystallized) soluble mono-

calcium phosphate and calcium sulfate (anhydrite), 196 parts of pure sulfuric acid and 18 parts of water are required, or 1 ton (2000 lbs) of the pure tricalcium phosphate requires 0.63 ton of sulfuric acid diluted with 0.06 ton of water. Such concentrated acid, however, contains 91.3 per cent H_2SO_4 and its volume is so small compared to that of the solid calcium phosphate that it would be impracticable to obtain a uniform mixture even if a substantial proportion of the water present were not driven off as steam during the ensuing violent reaction. It is customary therefore to employ much more dilute acid (from 65 to 73 per cent H_2SO_4) in order to insure a thorough mix and a complete reaction.

Since superphosphate made with acid of these later concentrations appeared to be a more or less self-drying product, it was generally believed that a considerable quantity of water was combined as gypsum $(CaSO_4 \cdot 2H_2O)$. Hill and Hendricks[9] however after examining the x-ray patterns of a number of products made in the laboratory as well as typical samples of superphosphate manufactured on a commercial scale, found that the vast bulk of calcium sulfate was present as anhydrite and conditions were unfavorable to the formation of gypsum.

Marshall *et al.*[16] found that both temperature and acid concentration have an important bearing on the form of calcium sulfate in superphosphate. Low temperatures and dilute acid favored the formation of gypsum $(CaSO_4 \cdot 2H_2O)$, but under ordinary factory conditions where acid having concentrations ranging from 65 to 70 per cent H_2SO_4 (52 to 56°Bé) and the temperature of the reaction is not dissipated by artificial cooling, anhydrite $(CaSO_4)$ is the normal form of calcium sulfate in the final product.

If less sulfuric acid is added to phosphate rock than that required to completely combine with two-thirds of the lime present, a certain amount of dicalcium phosphate is formed, which though not a water-soluble compound of lime and phosphoric acid, dissolves readily in neutral ammonium citrate solution and is generally recognized as available to crops. This reaction may be represented thus:

$Ca_3(PO_4)_2$ $+$ H_2SO_4 $+ 2H_2O$ $\rightarrow$
Tricalcium *Sulfuric Acid* *Water*
phosphate or B.P.L. (1 molecule, wt. 98) (2 molecules, wt. 36)
(1 molecule, wt. 310)

$CaSO_4$ $+$ $2CaHPO_4 \cdot 2H_2O$
Calcium sulfate *Dicalcium phosphate*
(1 molecule, wt. 136) (2 molecules, wt. 308)
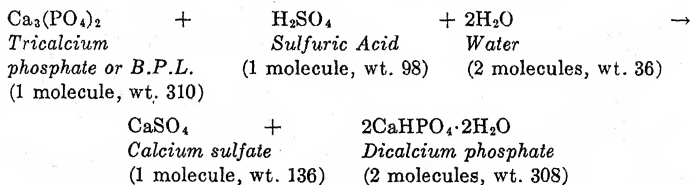
In order to insure a product free from uncombined phosphoric or sulfuric acid it is customary in factory practice either to add less sulfuric acid than that theoretically required to entirely convert the lime into monocalcium phosphate or to dust the superphosphate product with finely ground phosphate rock or limestone. In either case a small quantity of dicalcium

phosphate may be formed. Since this compound, however, answers the conventional tests for availability and full credit is allowed for such phosphoric acid in marketing superphosphate, it would seem logical from the standpoint of economy to employ only sufficient sulfuric acid to convert the phosphoric acid of phosphate rock into the dicalcium form.

With a view to manufacturing this intermediate product directly, repeated attempts have been made to cut the proportion of acid-to-rock normally employed, but very little success has been attained. The final product nearly always consists of a mixture of water-soluble monocalcium phosphate and residual or undecomposed phosphate rock.

This result is accounted for by the fact that tricalcium phosphate is very readily attacked by sulfuric acid, but the tendency of the reaction is to go to an end so that either phosphoric acid or monocalcium phosphate is formed. While phosphoric acid is an active reagent, monocalcium phosphate has rather weak acid properties and does not readily react with fluorapatite. Hence phosphate rock so treated always contains a high percentage of insoluble phosphoric acid even after it has been allowed to stand for a long period of time. It is entirely feasible, however, to produce dicalcium phosphate by treating superphosphate with limestone, or burned or slaked lime, and this has often been done where a prejudice exists against soluble phosphates because of their acid properties. Such practice, however is not economical since it involves additional mixing, handling and the further dilution of the final product. The manufacture of dicalcium phosphate from both bone and phosphate rock is discussed in Chapter 19.

Organic Matter

Since practically all the phosphates with the exception of igneous apatite are sedimentary deposits most of them contain a certain amount of organic matter. In the case of our Western phosphates and some of the phosphate deposits of Tennessee the content of organic matter is quite appreciable. On treatment with sulfuric acid the organic matter is partially oxidized and reduces the acid to sulfur dioxide (SO_2) and sometimes to hydrogen sulfide (H_2S). This means, of course, a consumption of acid and the evolution of gases that are not only objectionable but more or less deleterious to health.

The phosphate rock from some of the deposits in the western states is often calcined at high temperatures before treatment with sulfuric acid but even the ordinary drying operation to which most phosphate rock is submitted prior to acidulation, reduces the organic content appreciably. Because of the difficulty in ascertaining in just what form the organic matter occurs in phosphate rock it is not possible to predict what amount of acid it will consume except by actual trial test.

Silica and Silicates

The chief impurities found in many mineral phosphates are silica and silicates. The silica content of certain types of medium-grade phosphate rock suitable for the manufacture of superphosphate runs as high as 15 per cent. The presence of these impurities, however, is not considered objectionable except insofar as they dilute the mineral and render it more difficult to grind. They do not consume appreciable quantities of sulfuric acid. Silica, however, plays an important role in thermal methods of producing phosphorus and phosphoric acid; in fact, advantage is taken of their presence to bring about certain desired reactions and thus many phosphate deposits so high in silica as to be economically unsuited for the manufacture of superphosphate can thus be readily utilized.

These thermal methods of treating phosphate rock are described in Chapter 10.

Calcium Fluoride

As previously stated, fluorine is present in virtually all phosphate rock combined with lime in the apatite molecule $(3Ca_3(PO_4)_2 \cdot CaF_2)$. According to Jacob *et al.*[11] many phosphate deposits contain an excess of fluorine over that theoretically required for fluorapatite and this excess is present as fluorite (CaF_2). Most of the phosphate rock mined in the United States and North Africa contains from 3.1 to 4.2 per cent of fluorine (equivalent to 6.4 to 8.7 per cent CaF_2).

For practical purposes the fluorine may be considered combined as calcium fluoride and the first and main reaction taking place between this compound and sulfuric acid may be quantitatively represented thus:

$$CaF_2 \qquad + H_2SO_4 \qquad \rightarrow$$
Calcium Fluoride   *Sulfuric Acid*
(1 molecule, wt. 78)   (1 molecule, wt. 98)

$$CaSO_4 \qquad + \qquad 2HF$$
Calcium Sulfate   *Hydrofluoric Acid*
(1 molecule, wt. 136)   (2 molecules, wt. 40)
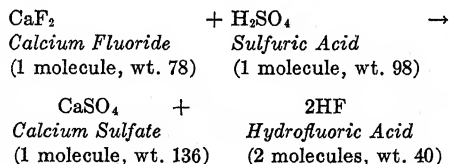
Most of this hydrofluoric acid (HF), however, acts upon the silica present in the rock as follows:

$$4HF \qquad + SiO_2 \qquad \rightarrow$$
Hydrofluoric Acid   *Silica*
(4 molecules, wt. 80)   (1 molecule, wt. 60)

$$SiF_4 \qquad + 2H_2O$$
Silicon Tetrafluoride   *Water*
(1 molecule, wt. 104)   (2 molecules, wt. 36)
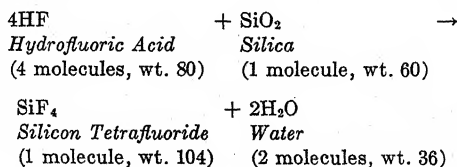
The silicon tetrafluoride, which is a gas, is decomposed in turn by water

with the formation of silica and hydrofluosilicic acid, thus:

$$3SiF_4 \quad + \quad 2H_2O \quad \rightarrow$$
Silicon Tetrafluoride   *Water*
(3 molecules, wt. 312)   (2 molecules, wt. 36)

$$SiO_2 \quad + 2H_2SiF_6$$
Silica   *Hydrofluosilicic Acid*
(1 molecule, wt. 60)   (2 molecules, wt. 288)
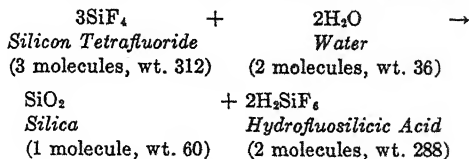
Before this last reaction takes place, however, a considerable amount of silicon tetrafluoride escapes as a gas and in treating mineral phosphate high in fluorides it is customary to pass the gases through spray towers or flues to decompose this compound and absorb the resulting hydrofluosilicic acid. This was done originally because these gaseous compounds of fluorine were a menace to the health of the laborers about the plant, were injurious to vegetation and a pronounced nuisance to surrounding communities. As in a number of other cases where the abatement of a nuisance was forced upon the manufacturer, the collection of fluorine gases has resulted in the production of valuable compounds. The hydrofluosilicic acid thus collected is employed in the manufacture of fluosilicates which have wide industrial applications.

The nature and proportion of the free acids of fluorine remaining in freshly prepared superphosphate depend to a considerable extent on the concentration of the sulfuric acid employed and the temperatures attained during acidulation of the rock. Hill and Beeson[3] state that hydrofluoric acid appears to be the predominant free fluorine acid in fresh superphosphate, although they recognize that small quantities of fluophosphoric acid (H_2PO_3F) and hydrofluosilicic acid (H_2SiF_6) may be present.

When sulfuric acid containing only 62 to 65 per cent H_2SO_4 (50 to 52°Bé) is used to decompose phosphate rock, only about 25 per cent of the fluorine is evolved, the balance remaining in the superphosphate; but with acid concentrations ranging from 69.7 to 72.8 per cent H_2SO_4 (55 to 57°Bé) considerably more fluorine is driven off.

The fact that higher conversions of the insoluble P_2O_5 into an available form are often obtained when phosphate rock is treated with less concentrated sulfuric acid indicates that the acids of fluorine remaining in the superphosphate have a solvent effect on the residual rock. This slight economy in the sulfuric acid requirements however must be balanced against the additional H_2SiF_6 recovered and the higher percentage of P_2O_5 in the superphosphate produced where the more concentrated sulfuric acid is employed.

Compounds of Iron and Aluminum

Iron and aluminum oxides, either in the free state or combined as phosphates, are objectionable impurities in phosphate rock to be used for

superphosphate manufacture[22]. Whereas, Jacob *et al.*[12] state that it is not definitely known whether or not iron and alumina play an important part in the formation of citrate insoluble P_2O_5 in superphosphate, it is generally believed that these impurities even when present in relatively small quantities cause a certain amount of reversion in the final product and when present in large amounts they are likely to produce a sticky superphosphate difficult to handle and distribute uniformly in the field.

The iron in natural phosphates may be conveniently represented by the formula $FePO_4$, although actually some of it may be in the form of oxide. The exact reactions which take place when this impurity is treated with sulfuric acid are not known, but unquestionably the iron is distributed between the two acids (H_3PO_4 and H_2SO_4). The general course of the reactions, however, is sufficiently well known to justify the assumption that they proceed mainly according to the following equations:

$$2FePO_4 \qquad + 3H_2SO_4 \qquad \rightarrow$$
Iron Phosphate   *Sulfuric Acid*
(2 molecules, wt. 302)   (3 molecules, wt. 294)

$$Fe_2(SO_4)_3 \qquad + 2H_3PO_4$$
Iron Sulfate   *Phosphoric Acid*
(1 molecule, wt. 400)   (2 molecules, wt. 196)
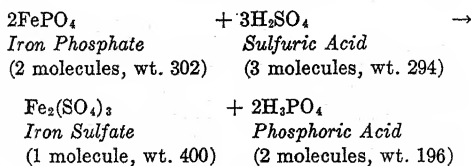
The reaction, however, indicated above is more or less reversible and in the presence of water hydrated phosphate of iron is formed as a gelatinous precipitate thus:

$$Fe_2(SO_4)_3 \quad + 2H_3PO_4 \qquad + 4H_2O \quad \rightarrow$$
Iron sulfate   *Phosphoric acid*   *Water*

$$2FePO_4 \cdot 2H_2O + 3H_2SO_4$$
Hydrated iron   *Sulfuric Acid*
phosphate
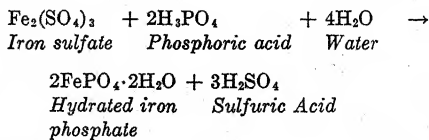
The hydrated iron phosphate is a slightly soluble, sticky, disagreeable compound which if present in relatively large amounts may impart objectionable physical properties to the entire product.

Fritsch[3] states that 2 per cent of iron oxide in phosphate rock is not objectionable because the quantity of iron sulfate produced therefrom remains unaltered in the superphosphate, but it appears very doubtful to the writers if he is right in this assumption. It seems much more likely that the complete or nearly complete solubility of the phosphoric acid in superphosphate made from rock high in iron and aluminum is due to the solvent effect of other compounds present, for Schneider[25] has shown experimentally that solutions of sulfate of iron increase the solubility of iron phosphate, and Cameron and Bell[1] have demonstrated that gypsum lime, and phosphoric acid also aid the solubility of this substance.

Hydrated iron phosphate, however, may be converted into the anhydrous

and even less soluble condition by reacting with anhydrous calcium sulfate, the latter compound being converted into gypsum as follows:

$$FePO_4 2H_2O + CaSO_4 \rightarrow CaSO_4 2H_2O + FePO_4$$

Hydrated iron phosphate *Anhydrous calcium sulfate* *Gypsum* *Anhydrous iron phosphate*
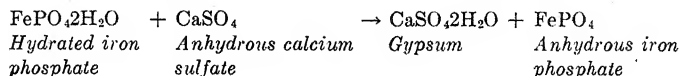
This last reaction may partly explain why superphosphate in excellent mechanical condition but with a relatively high percentage of P_2O_5 insoluble in water is often made from rock containing large amounts of iron and aluminum. Compounds of aluminum in phosphate rock react in a manner similar to those of iron, but to a less marked degree.

There is considerable difference of opinion regarding the maximum quantity of iron and aluminum which a phosphate rock may contain and still be successfully used for the manufacture of superphosphate. Wyatt[31] claims that phosphates containing from 6 to 8 per cent of iron and aluminum oxides may be used, providing there is sufficient carbonate of lime present to give a dry product. Schuecht[26] and Fritsch[3] seem to regard the presence of more than 3 per cent of the combined oxides of iron and aluminum as undesirable. Stillwell[9] states that phosphates containing from 4 to 6 per cent of these oxides may be successfully handled but that the presence of more than 2 per cent is objectionable. In actual factory practice, however, phosphate rock containing as high as 6 per cent combined oxides of aluminum and iron are being successfully worked up into superphosphate and though the handling of such phosphates necessitates experience, there seems little reason why they should not be employed if proper care is taken in their manipulation.

From the foregoing, it would appear that in treating phosphates high in compounds of iron and aluminum great care must be exercised both in the proportioning of acid and rock, and in the subsequent curing of the product to insure the absence of excess water or acid. Probably nothing has done more toward solving this problem than the adoption of modern methods for the mechanical excavation, aeration and careful drying of superphosphate.

The bulk of the phosphate rock employed in the manufacture of superphosphate contains a maximum of 4.5 per cent of iron and aluminum oxides and much of it contains 3 per cent or less of these impurities.

Carbonates of Lime and Magnesia

The presence of carbonates in relatively small quantities is considered by some as an advantage rather than an objection in the manufacture of superphosphate where a dry, readily handled product is of prime consideration. The carbonic acid is usually combined with lime and it is in this form that it is considered here. Sulfuric acid acts upon calcium carbonate

to form calcium sulfate, water or steam and carbon dioxide. The latter, which escapes as a gas, facilitates the elimination of moisture and renders the material porous and readily disintegrated. The reactions may be represented thus:

$$H_2SO_4 \quad + \quad CaCO_3 \quad \rightarrow$$
Sulfuric acid   *Calcium carbonate*
(1 molecule, wt. 98)   (1 molecule, wt. 100)

$$CaSO_4 \quad + \quad H_2O \quad + \quad CO_2$$
Calcium sulfate   *Water*   *Carbon dioxide*
(1 molecule, wt. 136)   (1 molecule, wt. 18)   (1 molecule, wt. 44)
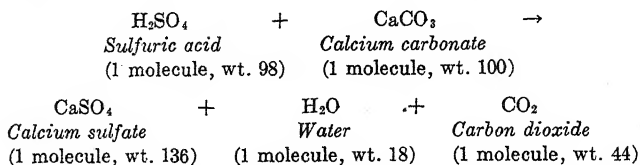
In acidulating phosphates high in carbonates, the reactions begin promptly in the mixing pan because of the ease with which carbonates are acted upon by sulfuric acid. This preliminary action tends to heat the mass, which facilitates the reactions between the acid and the other constituents of the phosphate rock. On the other hand, the acidulation of phosphate rock high in carbonates is not economical where better grades of this mineral are available. Not only is the quantity of sulfuric acid required to decompose calcium carbonate 60 per cent greater than that needed to convert an equal amount of tricalcium phosphate into soluble form, but the product ($CaSO_4$) of this reaction adds nothing to the sales value of the superphosphate.

Efforts have been made to decompose the carbonates present in phosphate rock before acidulation and thus cut down on the quantity of sulfuric acid, but no great amount of success has been attained. Memminger[19] proposed calcining pebble phosphate at a temperature sufficiently high to decompose the calcium carbonate and cause the lime to combine with the free silica to form calcium silicate. In this way the actual percentage of tricalcium phosphate may be increased 3 to 4 per cent, and since the calcium silicate is not readily attacked by sulfuric acid, an actual saving in the cost of acidulation is brought about. One of the objections raised to the use of this material, however, is that the absence of carbonates and partial sintering of the rock delays the action of the sulfuric acid unless the latter is heated to give the reactions an initial impetus. The other objection is that the lack of carbonates prevents the material from becoming porous due to the escape of carbon dioxide and hence the excess of water is not so readily driven off.

Shoeld *et al.*[28] recognizing the vital role that carbonates play as acid consuming impurities, studied six different grades of Florida pebble phosphate and developed a rapid method of determining the acid requirements based on the P_2O_5 and CO_2 content of such phosphate rock. By means of charts giving the percentage of these two ingredients present, they show in what proportions the acid and rock should be mixed to obtain super-

phosphate of any desired availability, as well as the most economical rock-acid ratio to employ.

Whereas, these investigators do not claim that this method is applicable to all classes of phosphate rock, it has proved satisfactory in plant practice on Florida rock where such factors as fineness of grinding, concentration and temperature of acid and length of curing period of the final product are kept constant.

Quantity, Strength, and Temperature of Sulfuric Acid

While the quantity, strength, and temperature of sulfuric acid, which should be used in treating phosphate rock to obtain superphosphate containing the maximum amount of available P_2O_5 and in the best mechanical condition, cannot be determined absolutely from the chemical composition of phosphate rock, nevertheless a close approximation may be made from the analysis of the phosphate which is to be acidulated.

As a specific instance of how the quantity of sulfuric acid (of various strengths) required may be fairly closely determined, let us take a sample of an average grade of Florida pebble phosphate, the composition of which is usually expressed in the following form (Table 10).

Since the main object in acidulating phosphate rock is to convert this phosphoric acid into an available form with due regard to the chemical action of the acid upon the other constituents in the material, the quantity of acid necessary may be approximately determined by calculating the amount required to satisfy the following equations, most of which have been previously given, but which are brought together here for the sake of clearness,

$$Ca_3(PO_4)_2 \quad + 2H_2SO_4 \quad \rightarrow CaH_4(PO_4)_2 + CaSO_4$$

(1 molecule, (2 molecules, (1 molecule, (2 molecules, (1)
wt. 310) wt. 196) wt. 234) wt. 272)

$$CaF_2 \quad + H_2SO_4 \quad \rightarrow 2HF \quad + CaSO_4$$

(1 molecule, (1 molecule, (2 molecules, (1 molecule, (2)
wt. 78) wt. 98) wt. 40) wt. 136)

$$2FePO_4 \quad + 3H_2SO_4 \quad \rightarrow Fe_2(SO_4)_3 \quad + 2H_3PO_4$$

(2 molecules, (3 molecules, (1 molecule, (2 molecules, (3)
wt. 302) wt. 294) wt. 400) wt. 196)

$$2AlPO_4 \quad + 3H_2SO_4 \quad \rightarrow Al_2(SO_4)_3 \quad + 2H_3PO_4$$

(2 molecules, (3 molecules, (1 molecule, (2 molecules, (4)
wt. 244) wt. 294) wt. 342) wt. 196)

$$CaCO_3 \quad + H_2SO_4 \quad \rightarrow CaSO_4 \quad + CO_2 \quad + H_2O$$

(1 molecule, (1 molecule, (1 molecule, (1 molecule, (1 molecule, (5)
wt. 100) wt. 98) wt. 136) wt. 44) wt. 18)

Taking the first equation shown to illustrate how the calculations are made in determining the amount of acid necessary for the treatment of this phosphate rock, it is seen that 196 parts by weight of pure sulfuric acid are required to convert 310 parts of tricalcium phosphate into the monocalcium or soluble form. Therefore, 0.632 parts of acid will be required for every part of tricalcium phosphate. If ordinary chamber acid (having a strength of 52° Bé) which according to Table 7 (the Appendix) contains 62.8 per cent of sulfuric acid, it is found that 1.016 parts by weight will be necessary for every one part of tricalcium phosphate.

In Table 11 the quantity of sulfuric acid of various strengths necessary to bring about the reactions outlined above is given.

Applying the figures given in Table 10 to the particular grade of rock under consideration it is an easy matter to determine the weight of acid

TABLE 10. ANALYSIS OF AN AVERAGE GRADE OF FLORIDA PEBBLE PHOSPHATE (DRY BASIS)

Ingredient	Composition* (%)
Calcium oxide (CaO)	46.7
Phosphoric acid (P_2O_5)	33.0
Carbon dioxide (CO_2)	3.4
Fluorine (F)	3.5
Ferric oxide (Fe_2O_3)	1.5
Alumina (Al_2O_3)	2.0
Silica (SiO_2)	10.0
Total	100.1

* This analysis does not include some of the minor constituents.

(of each strength) theoretically required to acidulate a hundred pounds of the phosphate. These values are given in part in Table 12.

The sulfuric acid requirements given in Table 12 are based on the assumption that all of the P_2O_5 contained in the phosphate rock is converted into a water-soluble form. The accomplishment of this end may be neither economical nor desirable because as the reaction proceeds the proportion of acid acting on certain impurities increases and the final traces of insoluble P_2O_5 are not attacked unless appreciable quantities of free acid are present. Not only may the cost of this extra acid required for complete conversion more than offset the additional value of the superphosphate, but the product is apt to be sticky and harden or set when stored or mixed with other fertilizer ingredients. In commercial practice therefore it is customary to use somewhat less sulfuric acid than is theoretically required and sacrifice a small amount of soluble P_2O_5 in order to insure a dry easily disintegrated product.

The strength of the sulfuric acid used also has an important influence on

the quality of the superphosphate. As pointed out previously, the amount of highly concentrated sulfuric acid theoretically necessary to produce superphosphate is of such small bulk that it is impossible to mix it thor-

TABLE 11. WEIGHT OF SULFURIC ACID OF VARIOUS STRENGTHS REQUIRED TO
CONVERT ONE POUND OF EACH OF THE INGREDIENTS OF AN AVERAGE
PHOSPHATE ROCK INTO THE COMPOUNDS EXISTING IN NORMAL
SUPERPHOSPHATES

Material Acidulated-Ingredient	Quantity and Strength of Acid Required (lbs.)								
	48° Bé	49° Bé	50° Bé	51° Bé	52° Bé	53° Bé	54° Bé	55° Bé	56° Bé
Tricalcium phosphate ($Ca_3(PO_4)_2$)	1.060	1.040	1.016	0.992	0.970	0.948	0.927	0.907	0.889
Calcium fluoride (CaF_2)	2.117	2.067	2.019	1.972	1.928	1.885	1.843	1.803	1.764
Iron phos. ($FePO_4$)	1.640	1.601	1.564	1.528	1.494	1.460	1.428	1.397	1.367
Aluminum phos. ($AlPO_4$)	2.030	1.932	1.936	1.893	1.848	1.807	1.767	1.728	1.693
Calcium carbonate ($CaCO_3$)	1.652	1.613	1.576	1.539	1.504	1.471	1.438	1.407	1.377

TABLE 12. QUANTITIES OF SULFURIC ACID REQUIRED (THEORETICALLY) TO
CONVERT 100 PARTS OF AVERAGE PEBBLE PHOSPHATE INTO
SUPERPHOSPHATE

Components of Rock (Arbitrarily Combined)	Quantity Present (%)	Quantities of Sulfuric Acid of Various Concentrations Per 100 Parts of Rock				
		48°Bé	50°Bé	52°Bé	54°Bé	56°Bé
Tricalcium phosphate ($Ca_3PO_4)_2$	67.4	71.4	68.5	65.4	62.5	59.9
Calcium fluoride (CaF_2)	7.2	15.2	14.5	13.9	13.3	12.7
Iron phosphate ($FePO_4$)	2.9	4.8	4.5	4.2	4.1	3.9
Aluminum phosphate ($AlPO_4$)	4.8	9.8	9.3	8.9	8.4	8.1
Calcium carbonate ($CaCO_3$)	7.7	12.7	12.1	11.6	11.1	10.6
Silica (SiO_2)	10.0					
Total	100.0	113.9	108.9	104.0	99.4	95.2

oughly with the ground phosphate rock; moreover, the calcium sulfate formed being less soluble in strong than in weak sulfuric acid, tends to coat the rock particles and prevent complete reaction from taking place. The heat generated also causes the loss of much of the water in the form of steam and this lack of liquid phase brings the reaction to a standstill.

On the other hand, if dilute acid is employed the amount required for decomposition of the rock is so large and contains such high percentages

of water that the mass does not heat up readily, chemical reaction is delayed, and even if finally complete, the product contains so much moisture that it must be dried by artificial means. The strength of acid with which the best results are ordinarily obtained ranges between 52 and 56°Bé, and in recent years there has been a tendency to use acid of the latter concentration since a somewhat higher grade superphosphate is thus obtained.

With a view to the recovery of a greater proportion of the fluorine present in phosphate rock, Wight and Tongue[30] propose adding highly concentrated, hot sulfuric acid to the finely ground material, pugging the plastic mass and subsequently diluting it with water to facilitate further mixing and more complete conversion of the P_2O_5 into an available form.

The temperature of sulfuric acid used also affects the speed of the reaction and the quality of the superphosphate produced though some manufacturers pay little attention to this point, mixing their rock at all seasons with the same weight of acid at whatever the temperature of the air may happen to be. In certain localities such practice may mean a difference of 100°F, between the temperature of the acid used in summer and in the winter months. Other manufacturers believe that phosphate rock should never be mixed with sulfuric acid which has a temperature lower than 75 to 80°F, and still others use acid at 120 to 180°F.

Sulfuric acid produced by the catalytic process may have a concentration of 100 per cent H_2SO_4 and even some of the so-called lead chamber acid contains close to 77.7 per cent H_2SO_4 (60°Bé). In either case such acid must he diluted with water which causes a sharp rise in temperature and may necessitate cooling the acid somewhat before using it in the manufacture of superphosphate.

While there is considerable difference of opinion regarding the optimum concentration and temperature of acid which should be employed, there are certain general rules which may be followed. Phosphates high in carbonates heat up quickly in the mixer and if care is not exercised, violent frothing is apt to occur and the pan will overflow. It is, therefore, unwise to use highly heated acid for such phosphates. On the other hand, phosphates high in iron and aluminum compounds, and those which have been calcined to the point where the carbonates are decomposed and lime silicates formed, react very much more sluggishly and, therefore, hot acid may be advantageously employed.

No definite formulas can be laid down which will apply to all grades of phosphate rock and no absolute rules made which will suit the different conditions under which the various factories operate. The best temperature, concentration, and quantity of acid to employ is more or less a separate problem for each individual plant and trial mixes are often necessary to

finally establish these points, but the manufacturer who does not exercise close supervision and chemical control over his raw materials and factory practice cannot possibly produce superphosphate as efficiently or as economically as one who gives strict attention to such important details.

Cost of Producing Superphosphate

The cost of producing superphosphate varies according to the size and location of the plant and its accessibility to supplies of raw materials. Plants situated at or near the Florida phosphate mines and where sulfur for sulfuric acid manufacture can be delivered at a relatively low figure, have an advantage as far as actual production costs are concerned over those located at inland points where long rail hauls on these raw materials are involved. On the other hand because of the high freight charges on superphosphate (per unit of P_2O_5), it is equally, if not more important that a manufacturing plant be built near large and established markets.

The bulk of the superphosphate plants in this country are either on or near the Eastern Seaboard where advantage is taken of the lower freight rates that prevail for both the raw materials and finished products shipped by water.

Plants that manufacture their own sulfuric acid are usually in a better position to compete in the market than those which must purchase this acid from other companies.

Tables 13 and 14 give the estimated capital investment required and the cost of producing ordinary superphosphate at a plant having a daily capacity of 1,000 tons situated at such a port as Baltimore, Maryland or Charleston, S. C., and equipped with modern facilities for handling, processing, storing and shipping both the raw materials and finished product.

The most striking features brought out by the figures given in Table 14 are that the raw materials (phosphate rock and sulphuric acid) constitute such a large percentage (92.7 per cent) of the cost of producing superphosphate, and that the direct manufacturing costs constitute such a small percentage (5.4 per cent).

There appears to be no prospect that the price of raw materials will be reduced in the near future and no possibility of decreasing the fixed charges (interest, taxes and depreciation). It is evident also that there is little opportunity of effecting substantial savings in labor, power, and supervision. If, therefore, any economy is to be brought about in the production of superphosphate, it must be effected by a substantial reduction in the proportion of sulphuric acid required to convert the P_2O_5 in a given quantity of phosphate rock into an available form.

As pointed out previously, if the reactions between phosphate rock and sulfuric acid can be so controlled that the predominating phosphate com-

pound in the resulting product is dicalcium rather than monocalcium phosphate, a great saving in the quantity of sulphuric acid required can be

TABLE 13. COST OF PLANT EQUIPMENT* HAVING A CAPACITY OF 1000 TONS OF SUPERPHOSPHATE PER DAY (330,000 TONS PER YR.)

Items	Cost
Plant site	$75,000
Loading and unloading facilities	300,000
Buildings for storage and equipment	300,000
Rock grinding mills and air separators (with motors)	100,000
Elevators and conveyors for rock	15,000
2 mixing pans (with motors) and weigh hoppers	20,000
2 mechanical dens and excavators	75,000
2 elevators for handling the den superphosphate	15,000
Trackage and cars	25,000
2 small steam shovels	50,000
Elevating, milling, and screening equipment	25,000
Total	$1,000,000

* Exclusive of sulfuric acid plant.

TABLE 14. ESTIMATED COST OF MANUFACTURING ORDINARY SUPERPHOSPHATE, (20% P_2O_5) AT PLANT ON ATLANTIC SEABOARD HAVING A CAPACITY OF 1000 TONS OF PRODUCT PER DAY (24 HOURS)

Items	Daily Cost	Proportion of Cost (%)
512 tons of H_2SO_4 (54°Bé) @ $8.50 per ton	$4,352.00	40.1
600 tons phos. rock (33% P_2O_5) @ $9.50 per ton	5,700.00	52.6
Grinding phosphate rock @ $0.50 per ton	300.00	2.7
Labor (8 men per shift) or 192 man hours @ $1.10 per hr	211.20	1.9
Superintendence	30.00	0.3
Maintenance and supplies	50.00	0.5
Power (9,000 kw-hrs) @ 0.6 cents per kw-hr	54.00	0.5
Depreciation on $1,000,000 @ 7½%	150.60	1.4
Total	$10,847.80	100.0
Cost per ton of 20% Superphosphate	$10.85	
Cost per unit of P_2O_5	$0.54	

effected. Even if only part of the tricalcium phosphate should be converted into dicalcium phosphate and the balance into monocalcium phosphate, there would still be a substantial economy in a process which could bring about such a result.

Although, this end has never been accomplished, the problem does not appear insurmountable and warrants further study.

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16. Concentrated or Triple Superphosphate

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Triple superphosphate, as its name implies, is a highly concentrated phosphate fertilizer containing from 45 to 50 per cent of available P_2O_5, or nearly three times as much as ordinary superphosphate (16 to 20 per cent P_2O_5). Since the main phosphate ingredient in these two products is the same, their chief difference is that triple superphosphate consists almost entirely of monocalcium phosphate[9], whereas in ordinary superphosphate this compound is diluted with a substantial proportion of calcium sulfate.

The manufacture of ordinary superphosphate as described in Chapter 15 is a relatively simple process which comprises mixing finely ground phosphate rock with proper proportions of sulfuric acid. The resultant mass is allowed to set up and is finally cured in large storage piles. In the production of triple superphosphate, however, phosphoric acid is used to decompose the phosphate rock and facilities must be provided to manufacture this acid.

An integrated plant for the manufacture of triple superphosphate not only entails a greater capital investment, but requires additional labor and processing which render the cost of the unit of P_2O_5 in this concentrate appreciably higher. Assuming that the reagents for manufacturing these two products are purchased in the form of sulfuric acid and electric energy, triple superphosphate requires twice as many steps as ordinary superphosphate, as shown in Table 1.

On the other hand, the higher cost of a plant producing this concentrate, and the additional processing steps and labor required, may be offset by the following favorable factors:

(1) The practicability of using (in the phosphoric acid production step) lower grade and cheaper phosphate rock unsuitable for the manufacture of ordinary superphosphate.

(2) The substantial economies effected in handling, bagging, shipping and distributing this more concentrated product.

Where deposits of phosphate rock and the reagents required to process

them are located far from established fertilizer markets, there is little question that triple superphosphate is a more economical product from the standpoint of both manufacturer and consumer.

TABLE 1. COMPARISON OF NUMBER OF STEPS INVOLVED IN THE MANUFACTURE OF
ORDINARY SUPERPHOSPHATE AND TRIPLE SUPERPHOSPHATE

Various Steps Involved	Ordinary Super-phosphate	Triple Superphosphate	
		Sulfuric Acid Process	Electric-Furnace Process
Manufacture of elemental phosphorus....................			×
Manufacture of phosphoric acid		×	×
Removal of gypsum............		×	
Concentration of acid..........		×	
Mixing of acid and rock........	×	×	×
Drying the product............		×	×
Final curing..................	×	×	×
Crushing and screening.........	×	×	×

TABLE 2. U. S. PRODUCTION OF TRIPLE SUPERPHOSPHATE (45% P_2O_5 BASIS)
(In Short Tons, 1939–1949)

Year	Production (Tons)
1939[a]	277,800
1940[a]	336,600
1941[a]	325,200
1942[a]	321,200
1943[a]	293,983
1944[b]	281,076
1945[b]	250,960
1946[b]	322,319
1947[b]	383,833
1948[b]	468,711
1949[b]	548,504
1950[b]	686,855

[a] U. S. Dept. of Agriculture figures.
[b] Figures of Bureau of Census.

The annual production of triple superphosphate in the United States from 1939 to 1949 inclusive is given in Table 2.

Triple superphosphate is now manufactured from phosphoric acid derived from the combustion of elemental phosphorus as well as through the medium of sulfuric acid. The main difference in these two acids is that the former is highly concentrated, almost free from contaminants, whereas the latter is relatively dilute and contains substantial percentages of impuri-

ties. Since both the concentration and purity of this reagent have an important bearing on the choice of equipment and procedure, the manufacture of triple superphosphate with each type of acid is discussed.

Manufacture of Triple Superphosphate through the Medium of Sulfuric Acid

Before electric-furnace and blast-furnace methods of treating phosphate rock were developed on an extensive scale, virtually all phosphoric acid was produced through the medium of sulfuric acid. When phosphoric acid thus obtained is used as a reagent in decomposing phosphate rock, it means that sulfuric acid is being indirectly employed.

The ratio of sulfuric-acid-to-rock used in the manufacture of ordinary superphosphate and triple superphosphate is substantially the same, and the nature of the phosphate compound (monocalcium phosphate) present is also identical. Therefore, were it not for the high concentration of triple superphosphate and the attendant economies in handling, shipping and distributing the product, there would be no incentive to produce it through the medium of sulfuric acid.

Although the P_2O_5 in almost all phosphate rock is combined as fluorapatite $(3Ca_3(PO_4)_2 \cdot CaF_2)$, the calcium fluoride (CaF_2) contained in the apatite molecule may be regarded as an acid-consuming impurity. The most important chemical changes in the manufacture of triple superphosphate are those involved in the conversion of tricalcium phosphate into water-soluble monocalcium phosphate. When the sulfuric acid process is employed these reactions may be represented in simplest form by the following equations:

$$2Ca_3(PO_4)_2 + 6H_2SO_4 + 12H_2O \rightarrow 4H_3PO_4 \quad + 6CaSO_4 2H_2O \qquad (1)$$
Tricalcic   *Phosphoric*
Phosphate   *Acid*
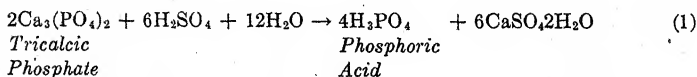
The strength of phosphoric acid thus produced ranges from 30 to 40 per cent H_3PO_4 depending on the procedure followed[16]. In any event, it must be separated from the gypsum and insoluble residue by filtration (Chapter 12), concentrated by evaporation and then used to treat a second batch of finely ground phosphate rock. No purification step other than filtration is employed in preparing acid for this purpose.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \quad + 3H_2O \rightarrow 3CaH_4(PO_4)_2H_2O \qquad (2)$$
Tricalcic   *Phosphoric*   *Monocalcic*
Phosphate   *Acid*   *Phosphate*
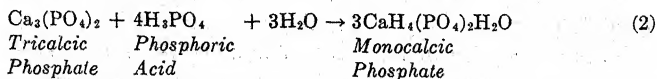
Because of the impurities present in phosphate rock, the reactions are by no means as simple as those given in equations (1) and (2). Unlike tricalcium phosphate these impurities consume phosphoric acid without

imparting any additional value to the product in the form of soluble P_2O_5. They are diluents at best and may actually have a deleterious effect on the chemical and physical properties of the final product. For instance, the presence of appreciable percentages of calcium and magnesium carbonates in phosphate rock is highly objectionable from the standpoint of extra acid consumed. Iron and aluminum compounds may adversely affect the solubility of the P_2O_5 in triple superphosphate or cause it to cake or set.

How best to determine the relative proportions of acid and rock used in the manufacture of triple superphosphate has been the subject of considerable discussion. A simple but not strictly accurate method is to mix the acid and rock in such proportions that the P_2O_5 added as acid is twice that of the rock. This method is based on the assumption that all the lime is combined as tricalcium phosphate and that the impurities do not consume appreciable quantities of acid. This, of course, is not the case.

Marshall *et al.*[10] in a study of the reactions between phosphate rock and various concentrations of phosphoric acid used an amount of acid 10 per cent in excess of that required to convert the calcium and P_2O_5 in the rock into monocalcium phosphate.

Another method is to determine the quantity of CaO in excess of that combined as apatite, and add sufficient acid to convert it into monocalcium phosphate. This method is also subject to inaccuracies.

Marshall and Hill[11] proposed an acidulation scale based on complete conversion of the CaO, Al_2O_3 and Fe_2O_3 present into $CaH_4(PO_4)_2$, $AlPO_4$ and $FePO_4$ respectively with due allowance being made for the acidic radicals such as P_2O_5, SO_3 and F. Such a scale, however, is dependent upon an almost complete analysis of the rock and is both tedious and expensive. The information furnished does not necessarily indicate the most economical practice to follow. It is often better to sacrifice a small percentage of available P_2O_5 in order to save on the quantity of acid used and to insure a product of optimum physical condition.

In a report by the engineering staff of the TVA[14] it is stated that a study of the reactions between rather pure phosphoric acid and several types of phosphate rock showed that as acidulation proceeds the proportion of acid acting on the insoluble P_2O_5 decreases, whereas the proportion consumed by the impurities increases. Side reactions therefore are set up before all of the P_2O_5 in the rock has been rendered available. This led to the conclusion that in order to obtain the maximum conversion of P_2O_5 into monocalcium phosphate it was necessary to use an excess of acid.

Not only is the presence of free phosphoric acid objectionable on account of the corrosive and hygroscopic properties it imparts to the final product, but the P_2O_5 in this acid is much more expensive than that in phosphate

rock. Unless it reacts with the latter, the cost of the triple superphosphate is increased without a corresponding increase in its value.

In general, less acid is needed to convert the P_2O_5 of high-grade phosphate rock into an available form[2], but each grade requires a different proportion of acid to obtain an optimum product. Although the approximate quantities can be determined by partial analysis, trial mixes have so far proved the most practical method of arriving at the proper acid-rock ratio.

According to equation (2) mixing 1 part of tricalcium phosphate $(Ca_3(PO_4)_2)$ with 1.26 parts of pure phosphoric acid, diluted with 0.17 part of water (equivalent to 87.8 per cent H_3PO_4), should yield 2.43 parts of dry, fully crystallized monocalcium phosphate.

It is economically impracticable, however, to mix such concentrated acid (or even 80 per cent H_3PO_4) with phosphate rock since the resultant mass sets up so rapidly that the two ingredients cannot be thoroughly blended and the reactions are incomplete.

Phosphoric acid produced by the sulfuric acid method is relatively dilute, ranging from 30 to 40 per cent H_3PO_4 (equivalent to 21.7 to 29.0 per cent P_2O_5). In manufacturing triple superphosphate it is usually concentrated to 60 to 70 per cent H_3PO_4 (47 to 50.7 per cent P_2O_5), either in Swenson evaporators or by percolation through acid-proof towers countercurrent to a stream of hot gases produced by combustion of oil or gas.

The description below is typical of the procedure followed in manufacturing triple superphosphate using finely ground phosphate rock (32 per cent P_2O_5) and phosphoric acid (50.7 per cent P_2O_5) produced by the sulfuric acid process.

Phosphoric acid (at a temperature of 140°F) and phosphate rock (80 per cent −100 mesh) are weighed in batches of 2,800 to 1,500 pounds respectively and added simultaneously to the pan of a 2-ton Steadman-type mixer. After thoroughly stirring the mixture for 3 minutes the plug in the center of the pan is raised and the slurry discharged directly into a bin or upon a wide conveyor belt (40 inches which carries it to an open reaction chamber where the material sets up into a fairly stiff mass. After several hours, it is picked up by a grab bucket and moved to another pile where it is allowed to cure for approximately three weeks. At the end of this period the triple superphosphate, which still contains about 15 per cent moisture, is taken to a drier (either of the rotary kiln or multiple-hearth furnace type) and dried to a moisture content of 2 to 5 per cent. The product is then cooled, crushed either in a hammermill or cage mill, screened and stored for final shipment. If a granulated product is desired, the dust and very fine particles are screened out or removed by an air separator, moistened to form pellets and again dried. In some cases the fine dust is added to the mixing pan and recycled through the system.

Meyers Process

With a view to eliminating the preliminary step of concentrating phosphoric acid and hastening the reaction, Meyers[12] patented a process for manufacturing triple superphosphate which he claimed is more efficient and economical than those previously used. The process has been modified a number of times since it was originally tried out on a commercial scale but in general the procedure is as follows:

Phosphoric acid is first produced by a continuous method consisting in mixing finely ground phosphate rock with sulfuric acid (60°Bé) diluted to 32°Bé, with weak phosphoric acid (15°Bé.), obtained in a subsequent step. The thin slurry flows continuously through a series of four decomposition tanks, each equipped with an agitator. No auxiliary heat is applied since the rise in temperature due to the dilution of the sulfuric acid is ample to complete the reaction.

The slurry is discharged from the fourth tank upon a moving filter belt (Lurgi filter) and the phosphoric acid is separated from the gypsum and insoluble residue by suction. The latter is then washed free of soluble phosphates and finally discharged at the far end of the filter bed.

Three concentrations of phosphoric acid are obtained:

(1) Production acid (30°Bé) resulting from the filtration of the slurry. This acid is subsequently used for manufacturing triple superphosphate.

(2) Dilution acid (15°Bé) resulting from the washing of the filter cake with 5°Bé phosphoric acid. This acid is used in diluting sulfuric acid in the initial decomposition of the phosphate rock.

(3) Washing acid (5°Bé.) resulting from the final washing of the filter cake with water. This dilute acid is used in the first washing of the filter cake. After passing through this cake it yields dilution acid (15°Bé.).

Triple superphosphate is then manufactured as follows:

Production acid (30°Bé) is mixed with finely ground phosphate rock in proper proportions to produce monocalcium phosphate. The relatively thin slurry is discharged into the upper end of the rotary kiln lined with fire brick heated cocurrently with powdered coal, oil or gas. The reaction between the acid and rock is hastened and rendered more complete because of the combined effect of the elevated temperature and gradual concentration of the acid as the material passes through the kiln.

The hot mixture, still in the form of a slurry, is discharged at the end of the kiln into a concrete container where it sets up as a porous mass. After 24 hours it is taken up by a crane and fed into a rotary (unlined) dryer and most of the free moisture is eliminated. The dried product is then crushed, screened and cured in a storage pile for several weeks before ship-

ment. This process has been successfully operated by the Armour Fertilizer Works in Florida and Tennessee.

Triple Superphosphate from Electric-Furnace Acid

The direct manufacture of pure concentrated phosphoric acid from elemental phosphorus evolved by smelting phosphate rock in an electric or blast furnace (Chapter 11) opened up new and interesting possibilities in the production of triple superphosphate. Such acid is much purer than that derived from the sulfuric acid process and it does not have to be concentrated by the application of artificial heat. A tedious and somewhat costly step is thus eliminated.

Marshall and his co-workers[10] investigated the action of phosphoric acid (ranging in strength from 21 to 64 per cent H_3PO_4) on phosphate rock under various conditions and found that acid of the maximum strength given above was more effective than lower concentrations. In curing the products, however, the water was not allowed to evaporate, and the effect of gradual concentration through loss of moisture was not determined in the products made with the weaker acid.

TVA later studied intensively the reactions between phosphate rock and higher concentrations of furnace grade phosphoric acid and has greatly advanced our knowledge in this field of research. These investigations are described in excellent papers[3, 4, 5, 6, 7, 8, 13, 14] by members of the technical staff of that agency. A detailed discussion of the difficulties encountered both in the laboratory and pilot plant need not be repeated here. However, a brief review of some of the highlights in the development of a practical process and descriptions of the equipment and procedures are of interest to all those who manufacture or are considering the manufacture of triple superphosphate from furnace-grade phosphoric acid.

Neither dilute nor highly concentrated phosphoric acid reacts as readily with phosphate rock as that of medium strength. As pointed out previously, 87 to 88 per cent H_3PO_4 contains only sufficient water to form fully crystallized monocalcium phosphate. Where an acid of 83 to 85 per cent concentration is employed the heat of the reaction will drive off much of the surplus water. In order to obtain maximum conversion of the insoluble P_2O_5 into an available form, not only should a substantial percentage of a liquid phase be present during the mixing period but a certain amount of moisture should be retained in the mass during the curing period to complete the reactions.

In mixing phosphate rock with highly concentrated acid (78 to 80 per cent H_3PO_4) the mass undergoes a number of successive physical as well as chemical changes. The TVA defines these physical changes as a fluid stage, a plastic stage and a solid stage. As the concentration of the acid used increases the duration of the first stage decreases.

Since most efficient mixing of the two ingredients takes place in the fluid stage, it is obvious if this period is shortened the individual particles of finely ground rock are less likely to be contacted with their proper quota of acid. Consequently, the chemical reactions are incomplete. With acid of the strength mentioned above the fluid stage was found to last only about 15 seconds. This is too short a period for thoroughly blending the two materials in the conventional type of mixer.

Batch Process[14]

In order to continue mixing during the plastic stage, heavy-duty Read sigma blade mixers of the tilting-type were installed equipped with 30 h-p motors. Scales with suspended hoppers and tanks for weighing the finely ground rock and acid were mounted over the mixers and provisions were
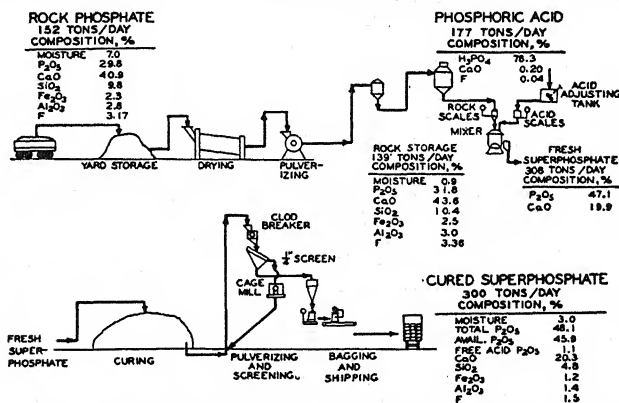
FIGURE 1. Flow diagram for superphosphate plant using batch mixing and storage curing.

made for diluting the 80 per cent acid to 78 per cent H_3PO_4. The acid was first introduced into the mixer and then the rock added in order to avoid immediate setting of the mass. Each batch was retained in the mixer for approximately 3 minutes but approximately 1 minute was an effective mixing period. The mixer was then tilted, dumped and the relatively dry set-up product discharged through a grizzly onto a conveyor belt and taken to the curing pile. The product was allowed to cure for a period of 3 to 4 months and then dug out by means of portable electric shovels. Dynamite was frequently used to loosen the set-up material so it could be handled by shovels. The cured superphosphate was then carried to a central hopper, discharged through a grizzly onto a belt conveyor, taken up by a bucket elevator, disintegrated in a cage mill, screened and bagged for shipment. A flowsheet of the triple superphosphate plant using this batch process is shown in Figure 1. The results obtained by this process are given in Table 3.

TABLE 3. COMPOSITION OF PLANT AND CONTROL SUPERPHOSPHATE MADE BY BATCH-MIXING—STORAGE-CURING PROCESS IN 1943

Month Made	Rock			Plant Superphosphate																	
				Fresh							Cured[1]						Acidulation		Conversion (MSH),[2] %	Acid Consumption, P₂O₅ from Acid/Avail. P₂O₅
	P₂O₅ (Dry Basis), %	P₂O₅/CaO Mole Ratio	Acid, % H₃PO₄	Free Acid, %	Total P₂O₅, %	Avail. P₂O₅ (MSH),[2] %	CaO, %	P₂O₅/CaO Mole Ratio	Conversion (MSH),[2] %	Acid Consumption P₂O₅ from Acid/Avail. P₂O₅	Curing Time, wk.	Moisture, %	Free Acid, %	Total P₂O₅, %	Avail. P₂O₅ (MSH),[2] %	CaO, %	P₂O₅/CaO Mole Ratio	P₂O₅ from Acid/P₂O₅ from Rock		
January	32.2	0.291	77.0	8.3	48.3	45.6	19.1	1.00	81	0.750	15	2.8	1.2	48.5	46.4	20.4	0.94	2.23	86	0.722
February	29.3	0.286	78.9	7.7	46.3	44.7	17.2	1.07	87	0.759	16	3.4	1.3	47.2	45.5	19.4	0.96	2.36	88	0.728
March	28.5	0.287	78.8	6.6	46.2	43.9	18.5	0.99	83	0.747	17	3.3	1.1	46.6	44.8	19.1	0.97	2.32	87	0.732
April	31.4	0.293	78.0	6.8	48.0	45.5	19.2	0.99	82	0.744	19	2.8	0.8	47.7	45.8	19.9	0.95	2.24	87	0.720
May	31.5	0.290	78.7	6.6	47.1	45.0	18.6	1.00	85	0.742	17	2.9	0.9	47.9	46.0	20.1	0.95	2.28	87	0.724
June	32.3	0.290	79.8	6.5	47.6	44.7	19.4	0.97	80	0.746	15	2.7	0.8	48.4	45.7	20.7	0.92	2.17	82	0.726
July	34.0	0.276	79.4	5.5	47.8	45.1	20.2	0.94	81	0.748	13	2.3	0.7	48.6	45.9	21.5	0.90	2.26	82	0.734
August	33.0	0.285	77.3	5.5	47.9	45.1	20.2	0.94	81	0.739	14	2.6	0.9	49.1	46.8	21.6	0.91	2.19	85	0.721
September	32.5	0.281	77.9	6.5	47.6	45.3	19.0	0.99	83	0.753	14	2.8	1.1	48.7	46.7	20.6	0.93	2.31	86	0.728
October	31.8	0.294	78.7	6.9	47.2	44.7	18.8	0.99	82	0.743	14	3.4	1.2	47.8	45.8	19.9	0.95	2.23	86	0.722
November	31.4	0.289	78.1	6.3	47.0	44.1	19.3	0.96	79	0.746	15	3.8	1.3	47.8	45.6	19.8	0.96	2.32	85	0.732
December	31.5	0.290	78.0	7.1	47.1	44.0	19.4	0.96	78	0.748	16	3.3	1.4	47.4	45.5	19.9	0.94	2.24	87	0.721
Average[3]	31.8	0.288	78.3	6.8	47.4	44.8	19.1	0.98	82	0.747	15	3.0	1.1	48.1	45.9	20.3	0.94	2.26	86	0.726

Control Superphosphate[4]

Fresh

Month Made	Moisture, %	Free Acid, %	Total P$_2$O$_5$, %	Available P$_2$O$_5$, % MSH[2]	Available P$_2$O$_5$, % A.O.A.C.	CaO, %	P$_2$O$_5$/CaO Mole Ratio	Conversion, % MSH[2]	Conversion, % A.O.A.C.	Acid Consumption,[5] P$_2$O$_5$ from Acid/Avail. P$_2$O$_5$
January	3.9	1.6	48.5	47.0	47.1	19.8	0.97	90	90	0.722
February	7.6	5.0	46.4	45.6	45.7	17.3	1.06	94	94	0.742
March	6.2	3.4	44.3	42.0	42.2	18.6	0.94	83	84	0.733
April	5.1	2.4	46.6	44.9	44.0	20.0	0.92	89	82	0.706
May	5.4	3.1	47.8	46.3	45.0	20.0	0.95	90	81	0.717
June	5.5	2.7	47.6	46.8	44.6	19.7	0.96	95	79	0.708
July	4.7	5.6	48.6	46.6	46.5	20.9	0.92	86	86	0.731
August	7.3	3.9	47.4	46.0	46.5	20.2	0.93	90	87	0.715
September	6.9	3.3	48.0	45.5	45.5	19.6	0.97	82	82	0.750
October	8.3	4.0	45.5	44.9	42.7	19.4	0.93	96	81	0.693
November	5.6	3.1	47.2	44.0	44.8	19.5	0.96	78	83	0.749
December	5.5	2.6	47.2	44.7	44.4	20.2	0.92	83	81	0.723
Average[3]	5.8	3.3	47.2	45.5	45.0	19.7	0.95	88	84	0.724

Cured

Month Made	Moisture, %	Free Acid, %	Total P$_2$O$_5$, %	Available P$_2$O$_5$, % MSH[2]	Available P$_2$O$_5$, % A.O.A.C.	Acidulation CaO, %	Acidulation P$_2$O$_5$/CaO Mole Ratio	Acidulation P$_2$O$_5$ from Acid/P$_2$O$_5$ from Rock	Conversion, % MSH[2]	Conversion, % A.O.A.C.	Acid Consumption,[5] P$_2$O$_5$ from Acid/Avail. P$_2$O$_5$
January	1.2	0.7	50.0	49.2	48.6	20.0	0.99	2.40	95	91	0.717
February	2.0	1.8	47.4	46.1	46.7	18.2	1.03	2.60	90	95	0.743
March	2.3	0.9	46.9	46.1	45.2	18.6	1.00	2.48	94	87	0.725
April	2.4	0.8	48.2	46.0	45.8	20.2	0.94	2.18	85	84	0.722
May	2.2	1.0	48.8	47.4	46.8	20.0	0.96	2.31	91	88	0.717
June	3.1	0.7	49.3	47.4	47.0	21.1	0.92	2.17	88	85	0.712
July	1.3	0.2	50.5	49.0	49.1	20.7	0.96	2.48	90	90	0.734
August	1.2	0.3	50.4	49.4	49.3	22.0	0.90	2.16	94	93	0.696
September	1.0	0.7	50.3	49.4	48.7	20.8	0.96	2.42	93	89	0.720
October	1.6	0.3	47.9	46.8	46.0	20.5	0.92	2.13	93	88	0.696
November	1.2	0.4	48.4	46.8	46.8	20.2	0.95	2.29	89	89	0.720
December	1.3	0.7	47.9	46.3	46.2	20.9	0.91	2.14	90	89	0.704
Average[3]	1.7	0.7	49.0	47.7	47.4	20.3	0.95	2.30	91	88	0.717

[1] Data for superphosphate made in corresponding month.

[2] MacIntire-Shaw-Hardin method. See "Equipment and procedure."

[3] Weighted on basis of superphosphate production.

[4] Made from corresponding monthly composite samples of acid and rock used in the plant.

[5] Calculated from MSH available P$_2$O$_5$.

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The data in Table 3 are taken from the engineering report of the TVA[14]. The upper section shows the results of plant operations with this batch process over a period of one year. The data include the grade of rock, concentration of acid, proportions in which these two materials were mixed, and the composition and availability of the fresh and cured product. The lower section gives similar data resulting from control experiments conducted in the laboratory. The somewhat better results obtained in the laboratory are attributed in part to more thorough mixing of this acid and rock and more favorable curing conditions.

Although the product thus obtained was fairly satisfactory, the power consumption, repairs and maintenance were excessively high and the output rather low (15 tons per mixer per hour of operating time). Frequent shut-downs for repairing and cleaning the equipment added appreciably to the cost of manufacturing triple superphosphate by this batch process and it was evident that a simpler and more economical scheme was required. After a long period of experimentation in the laboratory and on a plant scale a continuous method was devised and is now in successful operation.

Continuous Process

The development of this process is described in detail by Bridger and his co-workers[4, 14] but the outstanding feature is the type of equipment used in mixing phosphate rock with concentrated phosphoric acid.

The following is a condensed description of the installation and procedure, quoted from the latest report of this government agency[14].

"Acid Feeding System

Phosphoric acid from the acid plants was pumped to yard storage tanks where it was diluted from approximately 82 per cent H_3PO_4 to slightly above the desired concentration (usually in the range 74 to 78 per cent H_3PO_4). For final adjustment, it was then pumped to tanks mounted above the mixing unit, where liberal use of air for agitation was found helpful in accurate adjustment of acid strength. From these tanks the acid was fed by a constant-pressure centrifugal pump through a Fischer-Porter rotamatic acid flow controller-recorder (capacity 0 to 52,000 pounds per hour with a liquid specific gravity of 1.58) to acid-distributing nozzles in the mixer. All parts of this unit in contact with the acid were made of A. I. S. I. type 316 stainless steel. A removable strainer made of stainless steel was installed in the acid line ahead of the rotamatic controller, prevented large particles sometimes present in the acid from reaching the controller. The strainer was 4 inches in diameter and 30 inches long and had slot openings $\frac{3}{16}$ by $\frac{3}{8}$ inch in size. Compressed air was used for actuation in the controller. As a further refinement of acid flow control this compressed

air was passed through an alumina gel drier to prevent troublesome condensation of moisture from the air in the actuating mechanism. A recording thermocouple was installed for measurement of the acid temperature; a pressure regulator maintained the pressure in the acid line to the rotameter at about 23 pounds per square inch.

"When acid fairly free from suspended solids was used, rotameter performance was good. In test operation, the indicated quantity of acid fed by the rotameter was within 2 per cent of the amount calculated from volumetric measurements of the acid storage tanks. The instantaneous fluctuations of the recorder pin were within 1 per cent of the set value.

"**Rock-feeding system**—Rock phosphate (Tennessee rock, approximately 32 per cent P_2O_5) ground to about 80 per cent -200 mesh was conveyed intermittently from storage silos to a feed bin located above a Merrick Feedoweight constant-weight feeder (capacity, 6 to 18 tons per hour) which regulated the flow of pulverized rock to the mixer. Rock from the bin was delivered to the feeder through a 9-inch variable-speed screw conveyor designed to run full at all times. The speed of this conveyor was regulated by the feeder mechanism. Rock discharged from the feeder into a 6-inch screw conveyor inclined at 30 degrees with the horizontal, which delivered the rock to a vertical spout over the center of the mixing bowl. The inclined screw feeder was beneficial in smoothing out minor pulsations inherent in the feeder operation. Tests indicated that the amount fed by the feeder was within 2 per cent of the indicated value, and with unusually good calibration it was possible to reduce the error to within 1 per cent. A recording tachometer was used to assist in maintaining constant rates. Control of the rock level in the feed bin was maintained automatically by means of a level controller operated on an electrical capacitance principle.

"Mixer Bowl

The mixer consisted of an inverted truncated cone to which was attached a cylindrical extension at the bottom. Acid was introduced to the mixer through four 1-inch pipes spaced equidistant around the perimeter of the mixer. These pipes rested flat against the mixer walls and were adjustable, but normally they extended about 6 inches below the rim of the mixer. To each pipe was attached a 45 degree ell in which was fitted a standard $\frac{3}{4}$-inch pipe nipple serving as a nozzle. The nipples were turned flat against the mixer wall and they imparted to the acid a whirling motion along the side of the mixer.

"Rock was introduced into the center of the mixer bowl through a vertical spout extending to a level just below the acid nozzles. The rock fell into the vortex created by the tangential introduction of the acid to

the mixer. The fluid level was slightly above the mixer discharge extension, which was completely full at all times. The acid and rock appeared to be thoroughly mixed as they discharged from the mixer, and there was further opportunity for mixing on the belt conveyor receiving the effluent because of the turbulence there. There was no build-up of superphosphate in the bowl as there was in the earlier unit in which rock was introduced at the side of the mixer. Introduction of the rock into the vortex of acid was found to give the best operation and resulted in thorough mixing when sufficient holdup of fluid superphosphate in the mixer bowl was maintained. Under test operating conditions at 30 tons of superphosphate per hour the retension time in the mixer is estimated to be about 2 seconds, with a $2\frac{1}{2}$-inch diameter extension. Extensions 6 inches in length . . . were easier to rod out when this became necessary.

"A ventilating hood over the mixer removed fumes and the negatively small amount of dust arising from it. The major portion of the fluorine-bearing fumes was liberated along the length of the conveyor belt beneath the mixer. The belt was enclosed in a structure provided with doors for cleaning beneath the belt and with exhaust lines for removal of obnoxious fumes.

"Operation of the mixer began by starting first the rock to the mixer and then the acid. This procedure prevented acid from spilling on the conveyor belt.

"With precise control of the acid and rock rates to the mixer bowl this unit gave trouble free operation. The entire mixing unit was operated by two men."

A diagram of this mixer is shown in Figure 2.

"Belt Conveyor

The discharge from the mixer was received by a rubber belt conveyor running horizontally under the mixer. The center line of the mixer was approximately 6 feet from the center line of the tail pulley of the conveyor belt. The conveyor ran on troughing idlers and skirt boards about 4 feet long (made from pieces of discarded conveyor belt) were placed on each side of the conveyor under the mixer. A straight idler was installed approximately 6 to 10 feet from the center line of the mixer to flex the belt and cause the material to break apart. It would otherwise set up to a solid state by the time it reached this point In addition, a series of knives was used to cut the superphosphate into narrow ribbons about $1\frac{1}{2}$ inches wide.

"The conveyor belt used in the development of the continuous mixer unit was 36 inches wide and 37 feet between the center lines of the heads and tail pulleys. The belt traveled at a speed of 42.5 feet per minute, which provided a 45-second retention time for the superphosphate. With this belt

a maximum production capacity of 40 to 42 tons per hour of superphosphate could be maintained.

"Disintegrator

A squirrel-cage-type rotary disintegrator mounted above the conveyor belt at a point immediately over the head pulley shredded the superphos-
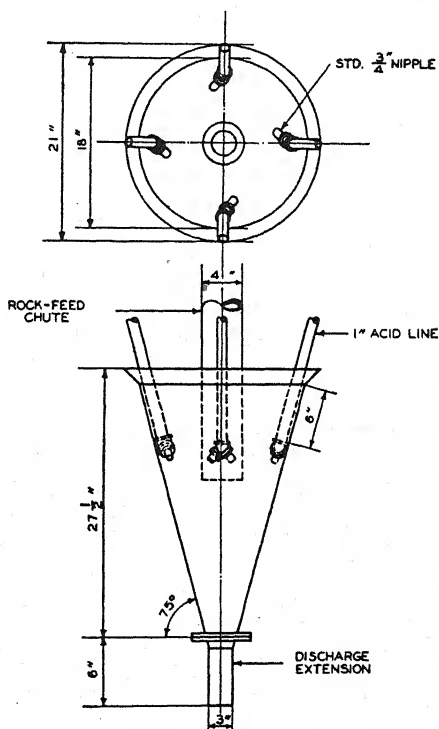
(Courtesy of TVA)

FIGURE 2. Sketch of continuous mixer.

phate as it was discharged from the conveyor belt. The disintegrator was 24 inches in diameter and extended over the full width of the conveyor belt. The disintegrator knives, 12 in number, were made of stainless steel, with beveled edges, and were parallel to the axis of rotation. The disintegrator was driven at 90 revolutions per minute by a 5-horsepower motor. Clearance between the edge of the knives and the surface of the conveyor belt was adjustable, but a distance of about 1 to $1\frac{1}{2}$ inches was found to give the best results. The disintegrator was housed in a box above the conveyor belt with built-in deflectors to direct the shredded product in the proper direction.

The disintegrator, which operated independently of the rest of the mixer unit, gave practically trouble-free operation and required very little attention.

Disintegration of the superphosphate resulted in the formation of considerable fines, depending on the mixing conditions, and practically complete elimination of lumps over 2 inches in size. This facilitated handling of the product, permitted the building of larger piles in the shed in which the material was stored for curing (because of a greater angle of repose of the disintegrated material), and greatly reduced the difficulties due to large, hard lumps when the cured superphosphate was ultimately ground for shipment.

"Performance

During the development of the mixer unit the acid concentration was varied from 72 to 80 per cent H_3PO_4, and the acid temperature was varied from 100° to 160° F. by means of a drip-type cooler. Good mixing was obtained in this range of acid concentrations and temperatures and was probably better at the lower concentrations, although this was not confirmed quantitatively. . . ."

"It was estimated that the mixing bowl used in this work would handle as high as 50 tons of superphosphate per hour with a 3-inch diameter extension, but because of limited retention time provided by the belt conveyor, a $2\frac{1}{2}$-inch-diameter extension and production rates between 40 and 45 tons per hour were used in most of the present work. Good operation of the mixer was not obtained at rates of 17 tons per hour and lower (using a $1\frac{3}{4}$-inch-diameter extension), because the flow of rock and acid was not sufficient to maintain the vortex action needed for good mixing and resulted in the mixer becoming plugged."

A flowsheet of the continuous mixing plant is shown in Figure 3.

"The advantages of the continuous-mixer process over the batch-mixer process are (1) it requires less operating labor, power, and maintenance; (2) it gives better mixing and therefore better P_2O_5 conversion than obtained with the batch-type mixers; (3) the investment required is less than that for the batch-mixing process; (4) control of the process can be made essentially automatic; and (5) considerably more flexibility is possible in operating conditions, such as acid concentration, acid temperature, and acid-rock proportion, which permits operation at conditions found to be optimum for P_2O_5 conversion. . . ."

"The chemical composition of cured superphosphates made from Tennessee brown rock phosphate (32 per cent P_2O_5) in the continuous-mixer plant and in the batch-mixer plant are compared in Table 4.

"A tabulation of some of the important operating indices for the two
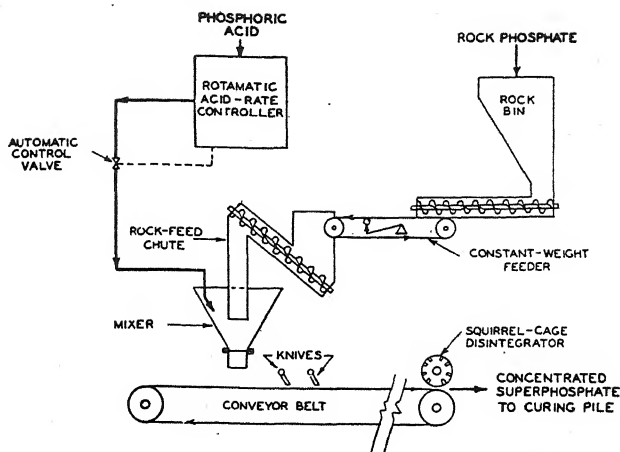
(Courtesy of TVA)

FIGURE 3. Flow sheet for continuous production of concentrated superphosphate.

TABLE 4

Mixer	Acid Used[1] (%) H_3PO_4	Acidulation, P_2O_5/CaO^2	Composition (%)				Conversion,[3, 5] (%)
			P_2O_5			Moisture[4]	
			Total	Available[3]	Free Acid		
Batch	78	0.94	48.1	45.9	1.1	3.0	86
Continuous	78	0.98	49.1	47.9	1.5	3.4	91
Continuous	75	0.98	48.5	47.5	2.0	5.1	93

[1] Acid temperature, 130 to 150°F.

[2] Mole ratio in product.

[3] M. S. H. method.

[4] Loss in weight over concentrated H_2SO_4.

[5] Percentage of rock P_2O_5 converted to available form.

TABLE 5. COMPARISON OF OPERATING INDICES FOR BATCH- AND CONTINUOUS-MIXING UNITS

	Batch Process	Continuous Process
Number of mixer units...............................	2	1
Production rate, tons superphosphate/operating hr[1].....	30	40
Power required, kw-hr/ton of superphosphate..........	1.0	0.1
Operating labor,[2] man-hr/ton of superphosphate........	0.16	0.04
Maintenance labor, man-hr/ton of superphosphate......	0.17	0.02
Maintenance materials, cents/ton of superphosphate....	9.7	0.9

[1] In addition, the percentage of scheduled time operated is much greater for the continuous process than for the batch process because less maintenance and clean-up are required.

[2] Includes foreman.

TABLE 6. CHEMICAL CONTROL DATA FOR CONTINUOUS-MIXING—STORAGE-CURING PLANT

Month Made	Rock				Fresh Superphosphate							Cured Superphosphate[1]							Acidulation	Conversion (MSH),[2] %	Acid Consumption, P2O5 from Acid/Avail. P2O5
	Source	P_2O_5 (Dry Basis), %	P_2O_5/CaO Mole Ratio	Acid, % H_3PO_4	Free Acid, %	Total P_2O_5, %	Avail. P_2O_5 (MSH),[2] %	CaO, %	P_2O_5/CaO Mole Ratio	Conversion (MSH),[2] %	Acid Consumption, P_2O_5 from Acid/Avail. P_2O_5	Curing Time, wk.	Moisture, %	Free Acid, %	Total P_2O_5, %	Avail. P_2O_5 (MSH),[2] %	CaO, %	P_2O_5/CaO Mole Ratio	P_2O_5 from Acid/P_2O_5 from Rock		
1946																					
January	Tenn.	32.0	0.280	82.0	10.4	49.2	45.3	18.9	1.03	72	0.789	19	2.6	1.3	49.4	47.7	20.5	0.95	2.39	89	0.730
February	"	31.7	0.290	77.7	7.6	47.9	45.8	18.8	1.01	85	0.745	18	2.5	1.2	49.1	47.2	20.9	0.93	2.21	88	0.719
March	"	32.3	0.286	76.1	6.3	47.2	45.5	19.0	0.97	88	0.731	18	2.9	1.1	48.6	46.8	21.0	0.92	2.17	88	0.715
April	"	32.2	0.286	75.4	6.7	47.5	46.0	18.6	1.01	89	0.739	19	3.0	1.3	48.5	47.2	20.6	0.93	2.21	89	0.717
May	"	31.9	0.280	75.6	6.8	46.6	44.8	18.7	0.98	87	0.743	19	3.3	1.7	49.0	47.0	20.1	0.96	2.43	92	0.727
June	"	32.5	0.282	75.2	6.8	46.4	44.7	18.9	0.97	88	0.743	18	4.1	1.9	48.6	47.0	19.7	0.97	2.46	91	0.730
July	"	32.0	0.284	75.2	7.0	46.0	43.9	18.8	0.97	85	0.739	16	4.6	2.0	48.0	46.7	19.5	0.97	2.46	91	0.727
August	"	31.6	0.280	74.9	6.6	46.5	44.8	18.5	0.99	88	0.744	15	4.9	2.1	47.9	47.2	19.3	0.98	2.50	94	0.726
September	"	31.5	0.284	74.8	6.7	46.8	45.5	18.7	0.99	90	0.732	15	4.9	2.1	47.6	46.8	18.9	0.99	2.54	91	0.724
Oct. 1-13	Florida	31.7	0.274	75.2	6.9	47.4	46.0	18.3	1.02	90	0.751	18	5.3	2.0	46.9	47.0	19.7	0.96	2.56	90	0.735
Oct. 14-30	"	31.1	0.274	77.0	5.9	47.4	45.7	18.9	0.94	88	0.733	18	5.9	2.3	47.1	47.4	18.7	0.97	2.59	89	0.743
November	"	30.8	0.263	77.0	6.5	47.4	46.2	19.3	0.97	91	0.746	16	6.0	2.3	46.9	47.5	18.7	0.99	2.81	92	0.751
December	"	31.2	0.265	77.4	6.1	47.6	46.1	19.5	0.96	89	0.747	15	5.5	2.4	47.7	47.3	19.1	0.99	2.81	91	0.749
Average[3]		31.6	0.278	76.4	6.8	47.2	45.5	18.9	0.98	88	0.743	17	4.4	1.9	48.0	47.1	19.7	0.96	2.43	91	0.731
1947																					
January	Florida	30.9	0.274	77.0	5.3	46.9	45.3	19.9	0.93	89	0.729	15	5.0	1.9	47.3	46.5	20.2	0.93	2.44	94	0.717
February	Tenn.	30.8	0.280	77.2	5.5	46.7	45.1	19.2	0.96	89	0.732	12	5.3	2.1	47.4	46.5	19.3	0.97	2.46	94	0.726
March	"	31.2	0.286	77.1	5.9	46.7	44.9	19.0	0.97	87	0.734	14	5.6	2.3	47.5	46.5	18.9	1.00	2.45	94	0.749
April	"	31.2	0.282	77.1	6.6	46.9	45.5	18.5	1.00	89	0.740	13	5.4	2.4	47.7	47.2	18.8	1.00	2.57	94	0.730
May 1-10	Florida	33.0	0.270	77.0	5.3	47.9	46.7	19.7	0.96	92	0.735	15	5.2	2.1	48.8	48.0	19.9	0.97	2.59	95	0.738
May 11-31	"	31.6	0.270	77.0	5.4	46.9	45.6	19.7	0.94	90	0.734	15	5.8	1.9	48.8	47.7	20.2	0.94	2.48	94	0.725
June	"	31.4	0.265	77.4	5.0	46.9	45.4	19.9	0.93	89	0.739	16	4.3	1.7	48.4	47.6	20.8	0.92	2.54	95	0.723
Average[3]		31.3	0.277	77.1	5.7	46.9	45.4	19.3	0.96	89	0.736	14	5.2	2.1	47.9	47.1	19.6	0.97	2.46	94	0.731

[1] Data for superphosphate made in corresponding month. [2] MacIntire-Shaw-Hardin method. See "Equipment and procedures." [3] Weighted on basis of superphosphate production.

types of unit, based on operating experience, is shown in Table 5. (These data are for proportioning and mixing only and do not include conveying of raw materials or product).

"Chemical control date for several months of operation of the continuous-mixing-storage-curing process are shown in Table 6. The moisture and free acid contents of the cured product were higher than for the batch-mixer product described in Table 3, because of the shorter curing time and higher acidulation used during the more recent period in which the continuous mixer was used. The conversions were higher for the continuous-mixed product, because of better mixing and higher acidulations. Acid consumptions were slightly higher for the continuous-mixed product even though conversions were also higher; this is due to the higher acidulations used."

Whereas this continuous process of manufacturing triple superphosphate is a notable development and a distinct improvement over the batch process formerly employed by the TVA, furnace-grade phosphoric acid is more costly than the crude acid obtained through the medium of sulfuric acid[1, 15].

So far, the bulk of the electric furnace acid (except that produced by TVA) has been consumed in the preparation of relatively pure salts for food and chemical purposes. However, if further developments render it practicable to produce such acid at a cost comparing favorably with that of crude acid obtained through the medium of sulfuric acid, there is little doubt that it will displace a substantial proportion of the latter in the manufacture of triple superphosphate and other concentrated fertilizers.

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17. Ammonium Phosphates and Ammoniated Superphosphates

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AMMONIUM PHOSPHATES

The potential value of ammonium phosphates as fertilizers has long been recognized. Use of orthophosphoric acid to fix either by-product or synthetic ammonia gives products in which both the acid and base have fertilizer value. Pure monoammonium phosphate contains 12.2 per cent nitrogen, 61.7 per cent P_2O_5, or a total of 73.9 per cent plant food. Diammonium phosphate contains 21.2 per cent nitrogen, 53.8 per cent P_2O_5, or a total of 75 per cent plant food. The advantage of such concentrated materials in respect to shipping, packaging, and handling costs renders them competitive in certain areas with ordinary fertilizer even though the production costs for the ordinary fertilizer may be less.

In ammonium phosphates a volatile base is combined with a relatively stable and nonvolatile acid. Heating converts ammonium phosphates into tacky masses. This property, coupled with their solubility, has led to extensive use of ammonium phosphates in fire-retardant compositions for impregnation of combustible materials.

Properties of Monoammonium Phosphate

Monoammonium phosphate crystallizes in the tetragonal system[62]. Crystallographic data are listed in Table 1. During World War II special techniques were developed for the growth of large single crystals of monoammonium phosphate, since its piezoelectric properties were utilized in high-frequency oscillators for electronic communications equipment[37].

Monoammonium is more stable than diammonium phosphate. The dissociation pressure of dry monoammonium phosphate is negligible up to 100°C and at 125°C it is only 0.05 mm of mercury[69]. Thermodynamic data for

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monoammonium phosphate are given in Table 2. The solubility relationships of the ammonium orthophosphates are represented in Figure 1 by the 0, 25, 50, and 75°C solubility isotherms of the ternary system

TABLE 1. CRYSTAL PROPERTIES OF AMMONIUM PHOSPHATES

	$NH_4H_2PO_4$	$(NH_4)_2HPO_4$
Crystal system......................	Tetragonal	Monoclinic
Optical characteristics................	Uniaxial negative	Axial angle 90°
Refractive indices		
Ordinary ray (Na D lines)........	1.5246[98]	
Extraordinary ray (Na D lines)..	1.4792[98]	
Alpha (white light)..............		1.508
Beta (white light)		1.516
Gamma (white light)		1.525
Specific gravity......................	1.803 at 19°C	1.619

TABLE 2. THERMODYNAMIC PROPERTIES AT 25°C

		$NH_4H_2PO_4$ (cryst.)	$(NH_4)_2HPO_4$ (cryst.)
Heat of formation...........	$\Delta Hf°$, kcal/mole*	−346.75	−376.12
Free energy of formation....	$\Delta Ff°$, kcal/mole	−290.46	
Entropy	$S°$, cal/deg mole	36.32	
Heat capacity..............	$Cp°$, cal/deg mole	34.0	43.5

Heats of formation in aqueous solution*

Moles H_2O per Mole of Salt	$\Delta Hf°$, kcal/mole	
	$NH_4H_2PO_4$	$(NH_4)_2HPO_4$
11		−374.07
20	−343.07	−373.96
30	−343.05	−373.82
40	−343.03	−373.71
50	−343.01	−373.63

* The increment in heat content (or enthalpy) associated with the reaction of forming the given compound from crystalline white phosphorus and from nitrogen, hydrogen and oxygen in a state of unit fugacity (1 atm.).

$(NH_3–HP_3O_4–H_2O)$[10, 54, 55, 68]. This figure indicates the existence of an ammonium phosphate more basic than diammonium phosphate and of another ammonium phosphate more acidic than monoammonium phosphate.

Figure 1 shows also that monoammonium phosphate dissolves congruently in water. The solubility of monoammonium phosphate in water at various temperatures is shown in Table 3. It is more soluble in dilute aque-

ous ammonia than in water or dilute phosphoric acid. The pH of a 0.1 molal solution is 4.38, which is alkaline to methyl orange and acid to methyl red[8]. The vapor pressures of saturated monoammonium phosphate solution and
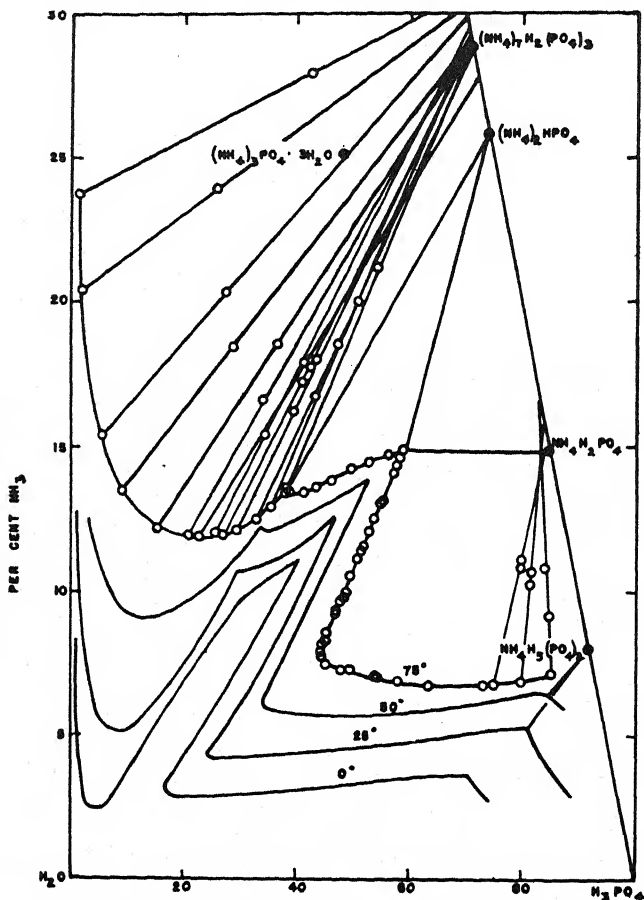
FIGURE 1. Solubility isotherms in the system NH_3-H_3PO_4-H_2O at 0, 25, 50, and 75°C.

the relative humidity of the air in equilibrium with it are given in Table 4.

In connection with its use in fertilizers, the particle strength of needle-like monoammonium phosphate crystals has been shown by shatter tests[64] to be satisfactory. Its drillability varies with the particle size distribution but is regarded as satisfactory[49, 64]. Pure monoammonium phosphate is

among the least hygroscopic of the soluble fertilizer salts; the relative humidity in equilibrium with its saturated aqueous solutions up to 40°C (104°F) exceeds 90 per cent, as shown in Table 4.

Compatibility of Monoammonium Phosphate. The stability and low hygroscopicity of monoammonium phosphate render it compatible with many

TABLE 3. SOLUBILITY OF MONOAMMONIUM PHOSPHATE AND OF DIAMMONIUM PHOSPHATE IN WATER

Temp. (°C)	$NH_4H_2PO_4$	$(NH_4)_2HPO_4$
	Grams per 100 grams water	
0	22.7	
10	29.5	62.8
20	37.4	69.0
25	40.3	71.0
30	46.4	75.2
40	56.7	81.8
50	68.0	89.2
60	82.5	97.3
70		106.0
75	108.8	108.7
80	118.3	
100	173.2	
110.5	215.0	

TABLE 4

Temp. (°C)	Vapor Pressure of Sat'd $NH_4H_2PO_4$ Solution (mm Hg)	Relative Humidity of Air in Equilibrium with Saturated Solution (%)
10	8.94	97.8
15	12.44	97.0
20	16.10	91.7
25	21.91	91.9
30	29.18	91.6
40	50.05	90.3
50	81.56	88.2

other fertilizer materials. Vapor pressures at 30°C (86°F) of aqueous solutions saturated simultaneously with monoammonium phosphate and with other primary phosphates, ammonium salts or urea are shown in Table 5. The relative humidities of the saturated solutions with and without monoammonium phosphate are also shown. These mixtures of monoammonium phosphate with other fertilizer salts having a common ion or with urea are relatively nonhygroscopic; in most cases the addition of monoammonium phosphate lowers the relative humidity over the saturated solution of the

other material by only a few per cent. Mixtures of 78 per cent monoammonium phosphate and 7 per cent ammonium sulfate (11 per cent N, 48 per cent P_2O_5) and of 32 per cent monoammonium phosphate and 59 per cent ammonium sulfate (16 per cent N, 20 per cent P_2O_5) were introduced into the fertilizer trade under the name "Ammo-Phos"[38]. These mixtures have outstanding physical properties and are relatively simple to manufacture. They show little tendency to cake in storage. Soluble salts which do not have any ions in common with monoammonium phosphate react with it in the presence of small amounts of water to form systems of reciprocal salt pairs[50]. Thus calcium nitrate reacts forming ammonium nitrate and monocalcium phosphate: $Ca(NO_3)_2 \cdot 4H_2O + 2NH_4H_2PO_4 \rightarrow 2NH_4NO_3 + Ca(H_2PO_4)_2 \cdot H_2O + 3H_2O$. According to the phase rule, both pairs of

TABLE 5. VAPOR PRESSURE AT 30°C OF SATURATED SOLUTIONS OF MIXTURES OF $NH_4H_2PO_4$ WITH OTHER FERTILIZER SALTS CONTAINING A COMMON ION OR WITH UREA[1]

Mixtures of $NH_4H_2PO_4$ with	Vapor Pressure of Sat'd. Soln., mm Hg	Relative Humidity of Air in Equilibrium with Sat'd Soln.	
		of Both Salts	of Added Salt Alone
		(%)	(%)
KH_2PO_4	28.99	91.0	92.9
$Ca(H_2PO_4)_2 \cdot H_2O$	28.26	88.8	93.7
$(NH_4)_2SO_4$	24.13	75.8	79.2
NH_4Cl	23.68	74.4	77.2
Urea	20.77	65.2	72.5
NH_4NO_3	18.46	58.0	59.4

salts can coexist in equilibrium with the saturated solution and its vapor only at one temperature. At any other temperature there can exist as a solid phase in equilibrium with the solution, vapor, and stable salt pair only one or the other member of the unstable salt pair. The occurence of solid solutions or double salts alters these relationships.

Table 6 shows fertilizer salts with which monoammonium phosphate forms stable salt pairs at 30°C (86°F). The compositions of the solid phases of the stable salt pair appear in column 2. Column 3 gives the solid phase of the unstable pair that forms upon addition of small quantities of water to the stable pair. The vapor pressure of the saturated aqueous solution and the relative humidity of the atmosphere in equilibrium therewith are shown in columns 4 and 5. Comparison of columns 5 and 6 shows how the addition of monoammonium phosphate lowers the equilibrium relative humidity from that of the saturated solution of the given salt alone to that of the equilibrium mixture shown. Despite the relatively low solubility of mono-

ammonium phosphate, its presence increases the hygroscopicity considerably in some of these cases.

In summarizing the data with respect to compatibility with other fertilizer salts, monoammonium phosphate may be said to be completely compatible with ammonium sulfate, potassium sulfate, calcium sulfate, monopotassium phosphate, and mono- and dicalcium phosphate. Its mixtures with urea, ammonium nitrate, and sodium nitrate are somewhat hygroscopic though not much more so than these substances by themselves. Potassium nitrate is among the least hygroscopic fertilizer salts, but its mixtures with monoammonium phosphate are about as hygroscopic

TABLE 6. FERTILIZER SALTS WITH WHICH $NH_4H_2PO_4$ FORMS STABLE SALT PAIRS[71]

Salt	Solid Phases Representing		Vapor Pressures of Sat'd. Solns. at 30°C	Relative Humidities of Air in Equilibrium with	
	Stable Salt Pair	Unstable Salt Pair		These Sat'd. Solns. (%)	Sat'd. Soln. of Salt Alone (%)
			mm Hg.		
$NaNO_3$	$NH_4H_2PO_4$; $NaNO_3$	$NaH_2PO_4 \cdot 2H_2O$	20.30	63.8	72.4
KNO_3	$(NH_4,K)H_2PO_4$;[a] $K(NH_4)NO_3$[b]	$NH_4(K)NO_3$[b]	19.03	59.8	90.5
K_2SO_4	$(NH_4,K)H_2PO_4$; $(K,NH_4)_2SO_4$[a]	(c)	25.16	79.0	96.3
$CaSO_4$	$NH_4H_2PO_4$; $CaSO_4 \cdot 2H_2O$	$Ca(H_2PO_4)_2 \cdot H_2O$	29.37	92.3	

[a] This formula represents a member of a complete series of solid solutions extending from one pure salt to the other.

[b] This formula represents a member of a series of solid solutions that does not extend continuously from NH_4NO_3 to KNO_3.

[c] There are only 2 solid phases in this system, but this is the point of maximum hygroscopicity and solubility.

as ammonium nitrate. To minimize bag-set, mixtures containing monoammonium phosphate and salts with which it forms reciprocal salt pair systems should be allowed to come to equilibrium prior to bagging. This is particularly true in cases as with potassium chloride with which it forms the unstable pair; the resulting pair is only moderately hygroscopic. Mixtures of monoammonium phosphate and calcium nitrate, especially when the latter is in excess, are extremely hygroscopic. Neutralization of the physiological acidity of monoammonium phosphate with limestone is undesirable, but dolomite may be used providing that overheating is avoided.

Methods of Manufacture

High-grade monoammonium phosphate can be made by absorption of anhydrous ammonia in phosphoric acid made from elemental phosphorus[64].

The process is of a continuous, single-stage saturator type similar to that used in the manufacture of by-product ammonium sulfate. By starting with 75 per cent phosphoric acid a pasty mass results from which crystalline monoammonium phosphate may be obtained by cooling, centrifuging, and drying. In crystallizing the product it is to be noted that the temperature coefficient of solubility of monoammonium phosphate is much greater than that of ammonium sulfate and that monoammonium phosphate crystals grow faster and have a greater tendency to knit together[62]. Moreover, if wet-process phosphoric acid is used, the precipitation of a considerable proportion of iron and aluminum phosphates as a gelatinous sludge presents complications not encountered in the manufacture of ammonium sulfate.

Fertilizer-grade monoammonium phosphate may be made batchwise from wet-process phosphoric acid and ammonia liquor from by-product coke manufacture[39]. The ammonia liquor is fed into the circulating batch of acid until the $NH_4H_2PO_4$ composition is reached. The concentrations of the reactants and the temperature are such that the resultant slurry can be pumped through pipelines. The product can be dried in a rotary oil-fired dryer.

A process for the continuous production of granular concentrated fertilizers[4] has been developed by the Dorr Company. According to Weber[68, 69, 70] this "process is especially attractive for the production of ammonium phosphate and is used by two of the largest producers of this type of product, one in Texas and the other in British Columbia.

"In this process, phosphoric acid or phosphoric acid mixed with sulfuric acid is neutralized with ammonia, essentially to monoammonium phosphate, blunged or mixed with a large quantity of previously produced granules and dried[41]. Only a very closely sized preferred fraction is screened out and the remainder, both oversize and undersize, circulates in the process. A very uniform, spherical, hard granule is produced. The entire production may be obtained as, for instance, −8 +10-mesh granules (2.4 to 1.7 mm).

"By varying the relative quantities of phosphoric acid and sulphuric acid used the N_2 to P_2O_5 ratio of the finished product can be varied from a straight monoammonium phosphate containing about 11 to 12 per cent nitrogen and 48 to 52 per cent P_2O_5 to pure ammonium sulfate with 21 per cent nitrogen. The intermediate products consist of mixtures of ammonium phosphate and ammonium sulfate to give analyses such as:

18–18–0, 16–24–0, 15–30–0, 14–35–0 and 13–39–0.

"The heat of neutralization is utilized to effect considerable evaporation of water so that the strength of phosphoric acid produced by the Dorrco Strong Acid Process (see Chapter 12) is sufficiently concentrated for use

in this process without evaporation and the evaporation station can be eliminated entirely.

"A simplified flowsheet of this process is shown in Figure 1A and Figure 1B illustrates a typical arrangement for a small plant.

"The phosphoric acid, or the mixed phosphoric-sulphuric acids, flow thru a series of agitators or saturators. The bulk of the neutralization is accomplished in the first agitator and the slurry is brought to the correct pH in the second and third agitators. The neutralized product is a thick slurry or a crystal magma.

"The mixer or so-called blunger consists of a trough shaped tank set on a slope and provided with two parallel horizontal shafts. These are equipped

Figure 1a. Dorrco ammonium phosphate process.

with overlapping angular blades and rotated towards each other so as to effect a very efficient mixing or fluidizing. A large amount of intermediate size dried granules are fed to the blunger together with a controlled amount of fine material derived from pulverizing any oversize granules and from the dust collecting system and drier cyclone. The slurry from the agitators is mixed with this dry material in the blunger. The granules are rolled and tumbled in such a way that they are given a thin uniform surface coating of wet slurry.

"This moistened product is then dried in a concurrent direct heat rotary drier. Due to the character of the feed, granular with only surface moisture, the drying is very rapid and the thermal efficiency is high.

"The product from the drier is conveyed and elevated to double deck screens. The material from between the screens is the finished product. The screen undersize is returned to the blunger as is also the screen oversize after pulverizing and any fines recovered from the drier gases and the

FIGURE 1b. Dorrco ammonium phosphate process typical layout of small plant.

dust control system. The drier gases before release to the atmosphere are water washed for removal of any fine dust and fluosilicates.

"The amount of dry material recycled to the blunger is of the order of 6 to 12 tons per ton of material produced so that in effect and on the average each granule produced is composed of 6 to 12 onion like shells or laminations which have been successively dried on initial crushed fragments or nuclei. The requisite number of nuclei, which determines the average size of the circulating material, is obtained by controlling the amount of material pulverized. The thickness of each layer is established by controlling the rate of recirculation and viscosity or thickness of the slurry produced in the agitators.

"The process is entirely continuous and can be designed and controlled to produce any reasonable desired size of granule. The granules are spherical and of remarkably uniform size."

Properties of Diammonium Phosphate

Diammonium phosphate is attractive for fertilizer use, owing to the comparatively high proportion of nitrogen-to-phosphorus that it contains and the high total plant-food content. The physical characteristics of the material that has been available, however, have discouraged the use of the product as a fertilizer in this country. Recently a new process has been developed which is reported to yield diammonium phosphate of satisfactory fertilizer properties.

Diammonium phosphate upon heating decomposes into ammonia and monoammonium phosphate. The dissociation pressure of the dry solid is about 5 mm of Hg at 100°C and 30.0 mm at 125°C[67]. Higher dissociation pressure has been indicated by Passille[58]. In the presence of its aqueous solutions diammonium phosphate exhibits a higher dissociation pressure, for the products in these circumstances are free ammonia and an aqueous solution unsaturated with respect to monoammonium phosphate[62]. Extrapolation of measured values of the vapor pressure of diammonium phosphate solutions extending up to 5 molal[28] indicates that for solutions saturated at 25°C (5.4 molal) the equilibrium partial pressures of ammonia and water vapor are about 1.06 mm and 21.1 mm respectively. This vapor pressure of ammonia from the saturated aqueous solution is about 100 times the calculated value for the dry salt at 25°C.

The solubility relations of diammonium phosphate as well as monoammonium phosphate are indicated by the data in Table 3 and the solubility isotherms of the ternary system NH_3–P_2O_5–H_2O shown in Figure 1.

Diammonium phosphate dissolves congruently in water at temperatures of 0 to 75°C[63] though a very slight excess of ammonia causes precipitation of a more basic phosphate which is less soluble than diammonium phos-

phate. The stability range of diammonium phosphate is much greater in the direction of monoammonium phosphate; solutions containing a NH_3/P_2O_5 mole ratio of 1.6 have been recommended for the crystallization of diammonium phosphate[64]. The pH of 0.1 molal solution of diammonium phosphate is 7.8[61]. Thermodynamic values of diammonium phosphate in the crystalline state as well as aqueous solutions are given in Table 2.

Diammonium phosphate offers advantage over monoammonium phosphate as a fertilizer material in that the fixing power of phosphoric acid for ammonia in the di-salt is twice that in the mono-salt. A form of diammonium phosphate recently developed by the TVA on a pilot-plant scale[64] was reported to have properties better than those of forms of the compound that were previously available.

Since the TVA product was obtained from a solution that contained excess phosphoric acid, the product contained from a few-tenths to several per cent of monoammonium phosphate equivalent, mostly distributed on the surface of the crystals. The individual crystals consisted of thin plates, octagonal in outline with a diameter about 10 times the thickness. A typical particle was formed from several plates bonded together by a film of crystallized mother liquor.

The major portion of the product, which approximated a 2:1 mole ratio of ammonia to phosphoric acid, absorbed comparatively little moisture at 80 per cent relative humidity. The product evidently can withstand exposure to normal atmospheres without excessive absorption of moisture.

Dry diammonium phosphate is sufficiently stable for wide general use. If considerable monoammonium phosphate is present there is less ammonia loss for a given proportion of moisture absorbed than in relatively pure diammonium phosphate, but this effect is offset by the greater tendency to absorb moisture. Dissociation of dry diammonium phosphate at 60°C is actually hastened by addition of monoammonium phosphate[1].

Caking tendencies of diammonium phosphate are comparable with those of monoammonium phosphate; both products may be regarded as satisfactory in this respect.

The drillability of TVA diammonium phosphate in fertilizer distributing equipment was found to be satisfactory[64] even when exposed at 80 per cent relative humidity for 24 hours. Inferior drillability was reported[43] for another form of diammonium phosphate that contained a wide range of particle sizes.

Compatability of Diammonium Phosphate with Other Fertilizer Materials. Mixtures of TVA diammonium phosphate plus muriate of potash with ammonium sulfate, superphosphate, triple superphosphate or monoammonium phosphate gave satisfactory results in caking, hygroscopicity, drillability and chemical stability[64] tests. Diammonium phosphate-muriate

of potash mixtures with sodium nitrate were satisfactory except for high moisture absorption at 35°C (95°F) and 83 per cent relative humidity. Mixtures containing diammonium phosphate plus muriate of potash and either ammonium nitrate or urea must be stored in moisture-proof containers, for they do not drill well if exposed to humid atmospheres. No loss of ammonia was observed from the mixtures with ammonium nitrate or urea that contained 0.5 unit of nitrogen per unit of P_2O_5, but decomposition occurred in mixtures of these materials that contained 0.75 and 1.0 units of nitrogen per unit of P_2O_5.

TVA tests showed that mixtures of diammonium phosphate that contained calcium cyanamid lost ammonia in storage[64]. Addition of limestone to render diammonium phosphate physiologically neutral resulted in high loss of ammonia at 30°C[7] from mixtures that contained 5 per cent moisture. Parallel tests with dolomite gave smaller but significant losses. Negligible NH_3 loss was observed from 4:1 mixtures of 100-mesh calcitic and dolomitic limestones with nitrophoska that contained 60 per cent diammonium phosphate even in the presence of 6 per cent moisture[48].

Methods of Manufacture

In most processes for the manufacture of diammonium phosphate, phosphoric acid is neutralized with ammonia in two stages. When wet-process phosphoric acid is used, the first stage of the introduction of ammonia results in precipitation of the bulk of the iron, aluminum, fluorine, calcium, and magnesium which are present. These impurities can then be removed by filtration. The filtrate which consists of a practically pure solution of monoammonium phosphate is evaporated and then saturated with ammonia to a NH_3/P_2O_5 mole ratio of 2:1. The product is crystallized, centrifuged and dried. The equipment required in this process is similar to that described for manufacture of the mono-basic salt. Diammonium phosphate solution is alkaline[69] and is not especially difficult to handle.

Several European plants employ a process[40] in which the heat of neutralization is utilized without loss of ammonia. By producing the monoammonium phosphate solution at its boiling point, the impurities are precipitated in a filterable form. The filtrate, after concentration in an evaporator, passes at its boiling point into an agitator where it is treated with more ammonia. The ammonia at first is absorbed almost completely by this solution while steam is liberated due to the heat of neutralization. When about half of the monoammonium phosphate has been converted into diammonium phosphate, the absorption is less complete and the escaping steam contains more ammonia. The mixture of ammonia and steam is used in another agitator in which the monoammonium phosphate solution is produced from wet-process phosphoric acid. The phosphoric acid solution

is preferably preheated to its boiling point before the ammoniacal steam is admitted. The steam generated in this stage of the neutralization can be utilized in preheating the acid.

Excess ammonia is used in the diammonium phosphate generator, since it serves to carry off considerable quantities of steam, thereby lowering the solution temperature from 110 or 115°C to 100°C or lower. Since at high temperatures diammonium phosphate is less soluble than monoammonium phosphate, much of the diammonium phosphate crystallizes out in the solution. The crystals are separated by centrifuging from the solution while it is hot or after cooling. The solid diammonium phosphate is dried at a moderate temperature and the solution is returned to the agitator with the next batch of monoammonium phosphate solution. The process can be operated also without the evaporator by using a series of agitators.

Furnace-process phosphoric acid (80 per cent H_3PO_4) may be added to diammonium phosphate mother liquor in a tank, or saturator, provided with a mechanical agitator[35]. By introducing gaseous ammonia the solution is brought to a 85:15 ratio of monoammonium phosphate to diammonium phosphate. Stirring is continued until the desired amount of water has been vaporized by the heat developed in the neutralization. The solution is discharged into a horizontal, water-jacketed, gas-tight rotary drum, further ammonia is added in the space in the drum above the solution until all the monoammonium phosphate is converted into diammonium phosphate. The charge is crystallized by continued rotation of the drum while it is cooled to ordinary temperatures by circulation of water through the cooling jacket. The crystals are removed by means of an Oliver filter and dried below 80°C (176°F) while the mother liquor is recycled.

The process developed by TVA for preparation of diammonium phosphate has not been published in detail. It consisted in continuous, single-stage saturation similar to that commonly used for manufacturing by-product ammonium sulfate[64]. Gaseous ammonia and concentrated phosphoric acid were fed continuously, at an $NH_3:H_3PO_4$ mole ratio of substantially 2.0 into a saturated solution of ammonium phosphate at about 60°C. Diammonium phosphate crystallized from the solution and was recovered by settling, centrifuging, washing and drying. The $NH_3:H_3PO_4$ mole ratio in the solution was maintained at about 1.6; the corresponding pH was about 6.0. This feature of the process is critical in preventing formation of unstable basic phosphates, and in minimizing the ammonia content of vapors escaping from the saturator. The crystals of diammonium phosphate which precipitated from this solution were wet with a film of the relatively acidic mother liquor, a portion of which was displaced by water during washing and the remainder of which crystallized on the diammonium phosphate crystals. The resulting product contained from a few-tenths to

several per cent of monoammonium phosphate equivalent, most distributed on the surface of the particles of the dibasic salt. This characteristic was believed to be peculiar to diammonium phosphate produced by this process, because most, if not all, other processes call for crystallization from solutions having $NH_3:H_3PO_4$ mole ratios close to 2.0.

·AMMONIATION OF SUPERPHOSPHATES

Introduction

Combination of superphosphate with aqueous or anhydrous ammonia or with ammoniacal solutions of nitrogen compounds increases the plant-food value of the product through use of low-cost and concentrated forms of nitrogen. The quantity of free ammonia added is commonly limited in commercial operation to a maximum of 30 to 40 pounds of ammonia per 1,000 pounds of superphosphate, or 0.123 to 0.164 unit of nitrogen per unit of P_2O_5. Quantities of total nitrogen several times this proportion may be incorporated in superphosphate by ammoniation with liquids that contain high ratios of total nitrogen to free-ammonia nitrogen. For example, use may be made of ammoniacal solutions that contain large proportions of ammonium nitrate, urea, or other highly soluble compounds which are rich in nitrogen. This provision of nitrogen in more than one type of chemical combination is frequently beneficial in respect to plant nutrition. Ammonium nitrate and urea are easier to produce and to handle as solutions than as solids. Ammonium nitrate introduced into a fertilizer in a dissolved state reacts more readily than solid ammonium nitrate with the potash salts in the mixture to form the less hygroscopic potassium nitrate and ammonium sulfate or chloride.

The free ammonia content of ammoniation solutions makes them efficient media for the quick curing of superphosphate. Fertilizer mixtures made in this way, if cooled to 38°C (100°F) or lower, can often be bagged and shipped within a few days after preparation. The neutralization of the acidity, moreover, reduces the chemical attack on bags.

Uniform distribution of the ammoniating solution throughout the fertilizer mixture tends to agglomerate the objectionable fine particles. Segregation and irregularities in composition are thus reduced and dusting and sifting of the mixture through the bag are minimized.

Solutions often supply in one operation all the nitrogen required in a complete fertilizer and otherwise added in several nitrogen carriers. Mechanical handling is simplified since the solution is commonly piped directly from tank cars or through storage tanks to the mixing machine and little labor is involved. The improved physical and chemical properties of ammoniated mixture reduce the degree of setting in storage and thus lower the handling costs,

History

In 1873 McDougal[45] patented the use of superphosphate as an absorbent for ammonia from illuminating gas; his process did not come into general use. Other patents relating to the absorption of gaseous ammonia in ordinary or concentrated superphosphate followed.

After the development of the synthetic ammonia process, ammonia began to be shipped to superphosphate plants in tank cars both as the anhydrous liquid and as aqueous solution. Much of the anhydrous ammonia was converted at the fertilizer plants into aqueous solution before use in ammoniation[20].

Control of the plant-food availability of the phosphate in ammoniated products through limitation of the addition of ammonia to 2 moles NH_3 per mole of water-soluble P_2O_5 was covered in a patent granted to Hagens and co-workers[15] in 1929. According to Ross and Merz[61] the consumption of free ammonia in fertilizer mixtures increased from 5,000 tons in 1928 to 40,000 tons in 1930.

In October, 1929, a solution of ammonium nitrate in ammonia, plus water, was used to ammoniate approximately 100 tons of superphosphate in a plant test at Norfolk, Virginia. This was the first commercial ammoniation of fertilizers with ammoniacal nitrate solutions, the type of ammoniation solution now most commonly used.

Chemistry of Ammoniation

In Absence of Sulfates. Although most fertilizer materials that are ammoniated contain sulfates, it is well to consider first the simpler reactions that occur in the substantial absence of calcium sulfate, as in the ammoniation of triple superphosphate made with phosphoric acid produced by oxidation of phosphorus. The principal reaction in all ammoniation of superphosphate is the conversion of water-soluble monocalcium phosphate into citrate-soluble dicalcium phosphate plus water-soluble monoammonium phosphate:

$$Ca(H_2PO_4)_2 \cdot H_2O + NH_3 \rightarrow CaHPO_4 + NH_4H_2PO_4 + H_2O \qquad (1)$$
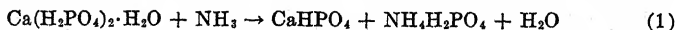
Reaction (1) represents the chemical change when one mole of free ammonia is added per mole of water-soluble P_2O_5. Expressed in other terms, this degree of ammoniation corresponds to 2.4 pounds of free ammonia per unit of water-soluble P_2O_5 or 6.8 per cent NH_3 in the product from pure monocalcium phosphate. The presence of free phosphoric acid with the monocalcium phosphate does not alter the products but merely increases the proportion of monoammonium phosphate. Because of the solubility of the reactants, reaction (1) proceeds rapidly in the presence of a minimum proportion of moisture.

If the addition of free ammonia is increased to 2 moles per mole of water-soluble P_2O_5, the monoammonium phosphate tends to be converted into diammonium phosphate:

$$NH_4H_2PO_4 + NH_3 \rightarrow (NH_4)_2HPO_4 \qquad (2)$$
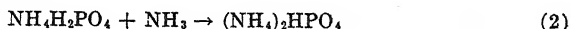
This reaction will occur at ordinary temperatures; it takes place at higher temperatures provided that sufficient pressure of ammonia is maintained to prevent decomposition of the diammonium phosphate. The overall effect of introducing 2 moles of free ammonia per mole of water-soluble P_2O_5 is given by the sum of reactions (1) and (2).

$$Ca(H_2PO_4)_2 \cdot H_2O + 2NH_3 \rightarrow CaHPO_4 + (NH_4)_2HPO_4 + H_2O \qquad (3)$$

In other terms this corresponds to addition of 4.8 pounds of free ammonia per unit of water-soluble P_2O_5, or production from pure monocalcium phoshosphate of a product containing 12.7 per cent NH_3. This represents the reaction of pure monocalcium phosphate with ammonia at ordinary temperatures[71].

At temperatures above 40°C (104°F) dicalcium phosphate reacts further with ammonia in a reversion into less soluble phosphates, represented conventionally as tricalcium phosphate. The other reaction product is diammonium phosphate[73].

$$3CaHPO_4 + 2NH_3 \rightarrow Ca_3(PO_4)_2 + (NH_4)_2HPO_4 \qquad (4)$$
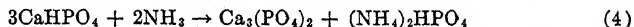
Combination of reactions (3) and (4) gives the over-all reaction:

$$3Ca(H_2PO_4)_2H_2O + 8NH_3 \rightarrow Ca_3(PO_4)_2 + 4(NH_4)_2HPO_4 + 3H_2O \qquad (5)$$
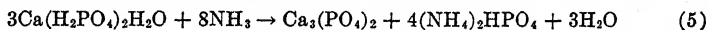
This corresponds to reaction of 2.67 moles of free ammonia per mole of water-soluble P_2O_5, 6.4 pounds of free ammonia per unit of water-soluble P_2O_5, or to an ammonia content of 16.2 per cent in the product from monocalcium phosphate.

The course of ammoniation in the absence of free phosphoric acid and calcium sulfate is illustrated in Figures 2 and 3. The indicated experimental points represent the results of addition of varying quantities of anhydrous ammonia under its normal vapor pressure at room temperature[71]. At 100°C (212°F) reactions (1), (2), and (5) take place successively and a product with a maximum ammonia content of 16.2 per cent may be obtained by slow reaction followed by cooling to ordinary temperature under ammonia pressure. At 25°C (77°F) the reactions are the same up to 12.7 per cent ammonia, which is the maximum absorption since reaction (4) does not occur under these conditions. Figure 4 shows what would happen theoretically if monocalcium phosphate, after treatment at 100°C (212°F) with various proportions of ammonia under pressure, is cooled slowly out of contact with ammonia so that the diammonium phosphate is completely
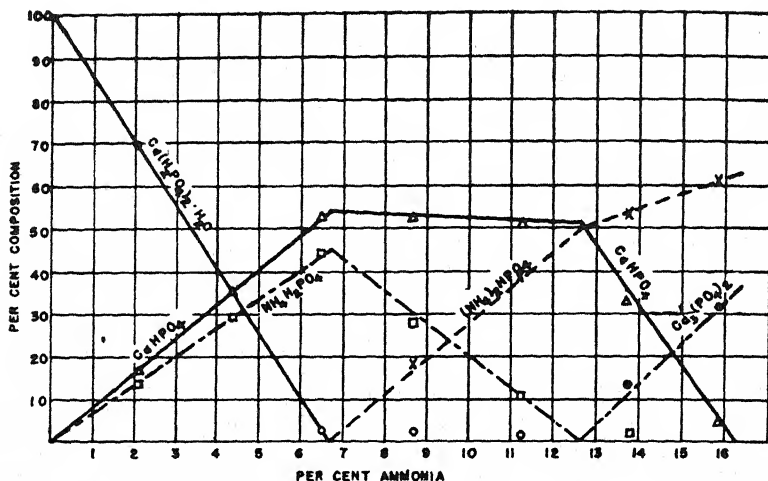
FIGURE 2. Composition of products obtained on ammoniating monocalcium phosphate at 100°C in a closed vessel.
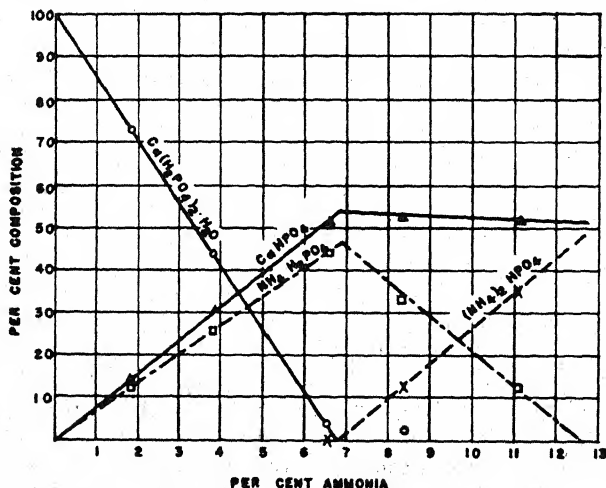
FIGURE 3. Composition of products obtained on ammoniating monocalcium phosphate at 25°C in a closed vessel.

decomposed. The maximum ammonia content of a product obtained in this way is 8.8 per cent and the proportion of tricalcium phosphate is relatively high.

Reaction (4), owing to the sparing solubility of dicalcium phosphate,

proceeds more slowly than reactions (1) and (2). The rate of absorption of ammonia by triple superphosphate is rapid at first; in ordinary commercial ammoniation about 70 per cent of the maximum quantity is absorbed within 2 minutes, but further absorption is slow[71].

Our knowledge of the products at high degrees of ammoniation is incomplete. The P_2O_5 reverts into forms less soluble than dicalcium phosphate but more soluble than the raw phosphate rock from which the triple superphosphate is derived. Hydrated tricalcium phosphate, hydroxyapatite, or both are probably among the products.
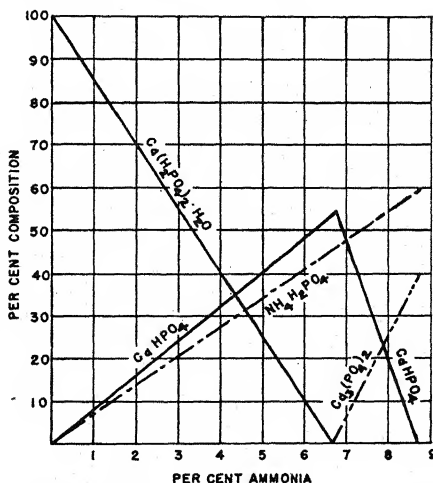
FIGURE 4. Composition of products obtained on ammoniating monocalcium phosphate at 100°C in a closed vessel with subsequent heating at 100°C in an open vessel.

In Presence of Calcium Sulfate. The presence in ordinary superphosphate of approximately 2 moles of calcium sulfate per mole of monocalcium phosphate does not materially affect the chemical reactions in the initial stages of ammoniation. Reaction (1) proceeds rapidly, and practically complete conversion of the monocalcium phosphate into dicalcium phosphate and monoammonium phosphate occurs upon addition of 24 pounds of neutralizing ammonia per 1,000 pounds of superphosphate of 20 per cent P_2O_5 content.

Absorption of the second mole of ammonia, however, does not lead simply to reaction (2), since diammonium phosphate reacts rapidly with calcium sulfate to form dicalcium phosphate and ammonium sulfate[15, 32].

$$(NH_4)_2HPO_4 + CaSO_4 \rightarrow CaHPO_4 + (NH_4)_2SO_4 \tag{6}$$

The sum of reactions (3) and (6) gives the over-all effect of adding two moles of free ammonia per mole of water-soluble P_2O_5[15] provided that occurrence of side reactions is excluded:

$$Ca(H_2PO_4)_2 \cdot H_2O + CaSO_4 + 2NH_3 \rightarrow 2CaHPO_4 + (NH_4)_2SO_4 + H_2O \quad (7)$$
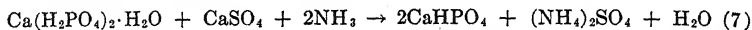
Reaction (7) corresponds to the addition of about 48 pounds of free ammonia per 1,000 pounds of 20 per cent superphosphate.

There is a possibility, however, that before reaction (6) or (7) is complete, some of the dicalcium phosphate may react simultaneously to form a more basic phosphate[15, 32] such as tricalcium phosphate which is only partially citrate-soluble:

$$2CaHPO_4 + CaSO_4 + 2NH_3 \rightarrow Ca_3(PO_4)_2 + (NH_4)_2SO_4 \quad (8)$$
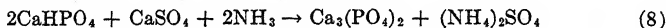
The maximum degree of ammoniation is represented by the summation of reactions (7) and (8), which corresponds to 4 moles of free ammonia per mole of water-soluble P_2O_5, or 96 pounds of ammonia per 1,000 pounds of 20 per cent P_2O_5 superphosphate:

$$Ca(H_2PO_4)_2 \cdot H_2O + 2CaSO_4 + 4NH_3 \rightarrow Ca_3(PO_4)_2 + 2(NH_4)_2SO_4 + H_2O \quad (9)$$
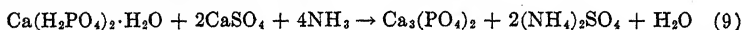
This degree of ammoniation cannot be reached under usual manufacturing conditions[31]. An ammonia content of 8 to 9 per cent may be attained by treating a superphosphate with a 25 to 30 per cent solution of ammonia or by passing ammonia into a superphosphate slurry and drying the product[61].

A graphic representation of the principal reactions in ammoniation of a superphosphate of negligible free phosphoric acid content is shown in Figure 5.

The course and extent of the reactions in highly ammoniated superphosphate depend upon the temperature and the amount of moisture in the mixture. Diammonium phosphate probably is formed as an unstable intermediate product which in turn reacts with calcium sulfate at a rate that varies with the temperature and moisture content[32]. The proportions of citrate-soluble and citrate-insoluble phosphates that result are dependent on the relative intimacy of contact of calcium sulfate and dicalcium phosphate with the highly ammoniated solution phase[30]. Momentary over-ammoniation can result in conditions of supersaturation of the solution phase with respect to dicalcium phosphate, tricalcium phosphate, and hydroxyapatite, simultaneously. The proportions in which these phases are precipitated may vary in an unpredictable manner owing to chance factors that influence the relative rates of crystallization. Hydroxyapatite, if precipitated in a temporary condition of over-alkalinity, is unlikely to pass back entirely into solution even though further agitation may equalize the pH of the solution phase at a relatively low value. Double sulfates such

as syngenite, $CaSO_4 \cdot (NH_4)_2SO_4 \cdot H_2O$, formed under some conditions, may account for the presence of water-insoluble nitrogen. Combinations of sulfate and phosphate such as ardealite, $CaSO_4 \cdot CaHPO_4 \cdot 4H_2O$, are possible[43].

The variation in composition of the products obtained by different degrees of ammoniation of triple superphosphate that contained 3.2 per cent of calcium sulfate on a dry basis is shown in Figure 6[71]. The material con-
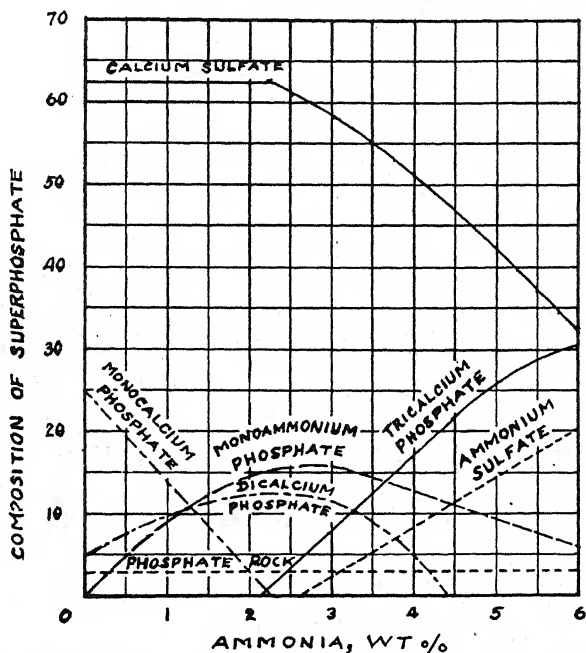
FIGURE 5. Change in composition of a superphosphate with increasing ammoniation.

tained initially 5.2 per cent free H_3PO_4 and 1.79 per cent SO_3. It was adjusted to a moisture content of 5 per cent and then ammoniated under pressure at 100°C (212°F). The products were allowed to stand for one month before being analyzed. It was assumed that the calcium sulfate did not react until all of the monocalcium phosphate had been converted into dicalcium phosphate, and that further addition of ammonia was accompanied by reaction of the calcium sulfate and formation of tricalcium phosphate and ammonium sulfate[3, 32] until the supply of calcium sulfate was exhausted. Formation of a small amount of tricalcium phosphate is indicated when the ammonia content exceeds 6.1 per cent, but major

formation of tricalcium phosphate does not begin until the ammonia content approaches 12 per cent.

When triple superphosphate is treated with ammonia in an open or partially closed vessel, little or no tricalcium phosphate is formed except for that which results from the calcium sulfate that may be present. There is negligible conversion of dicalcium phosphate into tricalcium phosphate according to reaction (4) at the partial pressures of ammonia existing in the reaction mass under these conditions.

Degree of Ammoniation. From the chemical reactions that occur in ammoniation it is clear that addition of excessive amounts of free ammonia
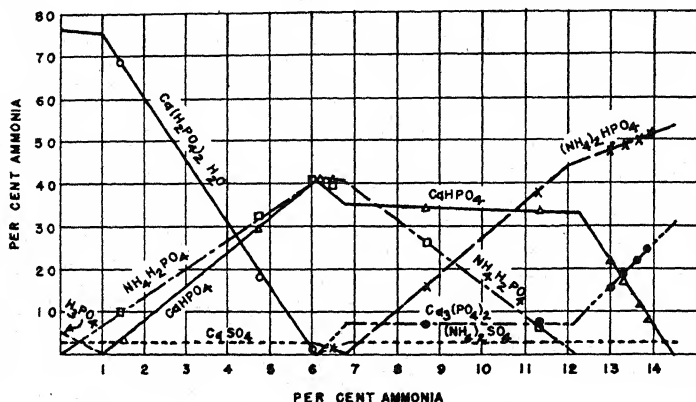
FIGURE 6. Composition of products obtained on ammoniating triple superphosphate at 100°C in a closed vessel.

to a superphosphate causes reversion into insoluble forms. It has frequently been observed in the fertilizer industry, however, that different superphosphates react differently[17]. The graphs in Figure 7 are illustrative of the published information relative to the trends toward decreased solubility with increasing degrees of ammoniation[33]. These graphs were based on experiments in ammoniating superphosphates that contained 7 to 8 per cent moisture, 18.7 per cent total P_2O_5, and 3 to 4 per cent free acid with anhydrous ammonia in a small drum mixer. The citrate-solubilities were determined by 60 minutes' extraction of 1-gram samples, as prescribed in the present official method of the Association of Official Agricultural Chemists. Other experiments in the same series showed that it is feasible to add considerably more ammonia in proportion to the superphosphate in fertilizer mixtures in which the P_2O_5 concentration is lowered by dilution of the superphosphate with other fertilizer materials. In practice,

there has been a trend recently to increase the degree of ammoniation beyond what was formerly regarded as the upper limit.

Heat of Ammoniation. In most fertilizer mixtures, increase in temperature accelerates reactions that cause reversion of soluble phosphates, decomposition of urea[42] and other easily decomposable materials, and loss of ammonia. The evolution of heat in ammoniation of representative types of superphosphate and triple superphosphate with varying quantities of liquid ammonia[16] is shown in Figure 8. The experimental determinations

(Neutralizing NH₃ in Superphosphate, %).
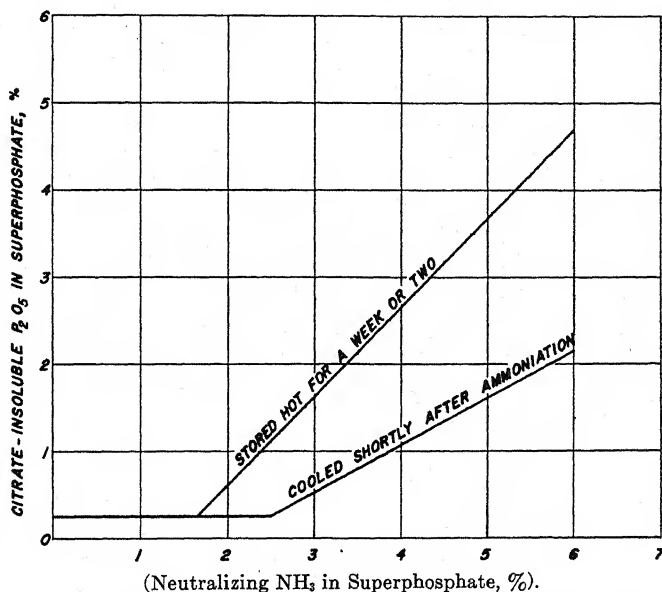
FIGURE 7. Trend in citrate solubility with increasing degree of ammoniation.

of the heats of ammoniation agree closely with values calculated from the heats of formation of the reactants and products.

From a knowledge of the heat developed by ammoniation and the heat capacities of the resultant products one may calculate the maximum temperature rise of any ammoniated product. Values of the heat capacity of fertilizer materials are given in Table 7. The use of these data in calculating the temperatures developed in ammoniation of superphosphate, triple superphosphate and mixtures as a function of the moisture content was illustrated in the original publication[16]. For example, when a superphosphate containing 5 per cent moisture is ammoniated with anhydrous ammonia at the rate of 28.5 pounds of ammonia for 1,000 pounds of super-

phosphate, the heat evolved is sufficient to raise the temperature of the mixture from 25°C (77°F) to 100°C (212°F) and to vaporize about 9 per
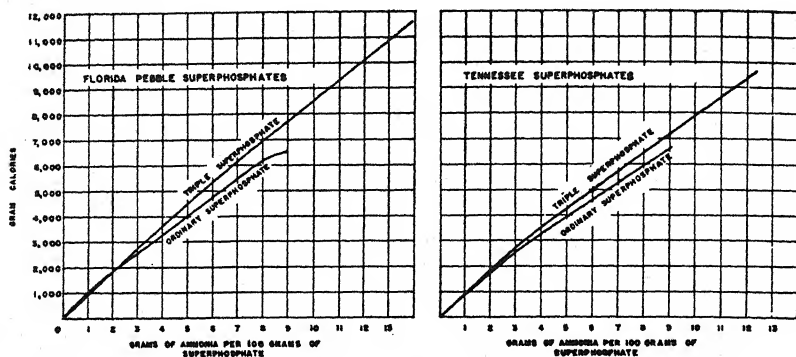
FIGURE 8. Heat developed on treating superphosphates with varying quantities of liquid ammonia.

TABLE 7. HEAT CAPACITIES OF SUPERPHOSPHATE, TRIPLE SUPERPHOSPHATE AND THEIR PRODUCTS OF AMMONIATION WITH ANHYDROUS AMMONIA

Material	NH_3 Added per 100 grams of Superphosphate	Heat Capacity at 27.6°C g.cal./(g.)(deg. C.)*
Florida pebble superphosphate........	—	0.207
Ammoniated Florida pebble super-phosphate.........................	2	0.234
Ammoniated Florida pebble super-phosphate.........................	3	0.235
Ammoniated Florida pebble super-phosphate.........................	4	0.248
Florida pebble triple superphosphate..	—	0.246
Ammoniated Florida pebble triple su-perphosphate......................	4	0.281
Ammoniated Florida pebble triple su-perphosphate......................	6	0.270
Ammoniated Florida pebble triple su-perphosphate......................	8	0.303
Single-strength mixture (4–9–5).......		0.229
Double-strength mixture (8–18–10)....		0.269

* Although the materials contained moisture, the results were calculated on the basis that the materials were moisture-free before ammoniation and that any water of hydration released in the ammoniation was retained.

cent of the moisture present. Similarly if a 4–9–5 mixture of the heat capacity indicated in Table 7 is prepared by ammoniation with anhydrous ammonia at the rate 27 pounds of ammonia per ton of mixture containing

5 per cent moisture, the temperature may be calculated to rise from 25°C (77°F) to 68°C (154°F). With commercial ammoniation solutions the temperature rise is less. The temperature rise in commercial mixtures ammoniated with a solution containing 60 per cent ammonium nitrate, 20 per cent ammonia, and 20 per cent water has been found to be about 0.94°C (1.7°F) per pound of neutralizing ammonia per ton of mixture[5]. A solution that contained 32.5 per cent urea, 28.9 per cent ammonia, 18.1 per cent ammonium carbamate, and 20.5 per cent water gave temperature increases of 18 to 14°C (33 to 25°F) per unit of added nitrogen, or 1.1 to 0.85°C (2.0 to 1.5°F) per pound of neutralizing ammonia per ton of mixture, as the proportion of solution was varied from 36 to 72 pounds or more per ton of 7–6–5 mixture[13].

Citrate Solubility

Effect of Storage. Reversion of P_2O_5 to citrate-insoluble form increases with increase in storage temperature and with duration of storage at elevated temperatures as shown in Tables 8 and 9. Small batches (2 kg) of commercial superphosphates from different sources were ammoniated with a solution containing 60 per cent ammonium nitrate, 20 per cent ammonia, and 20 per cent water at the rate of 30 pounds of free ammonia per 1,000 pounds of superphosphate[27]. Portions of the products were stored in stoppered bottles at various temperatures. Determinations of citrate-insoluble P_2O_5 were made at intervals by the Official Method of the Association of Official Agricultural Chemists, and also by a procedure identical in all respects except that the quantity of sample for analysis was reduced from 1 to 0.5 gram. The average percentages of the total P_2O_5 that reverted as determined by the official method in all the ammoniated superphosphates after 27 to 42 days' storage was 2.5 per cent at room temperature, 5.8 per cent at 40°C (104°F), 6.8 per cent at 50°C (122°F) and 10.3 per cent at 80°C (176°F).

The reversion in an ammoniated mixture, as shown in Figure 9, was roughly one-half that which occurs in ammoniated superphosphates[31] at comparable temperatures. The mixtures contained no dolomite or other neutralizing agents to compensate for the physiological acidity of the nitrogen carriers. It will be noted that at ordinary temperature (27°C) reversion was negligible throughout the 60 days of storage. At elevated temperatures significant reversion occurred even during the initial part of the storage period and continued throughout the test period.

Effect of Fluorine. Fluorine is generally present in superphosphates. Some investigators[47] have thought that reversion is due principally to the formation of fluorapatite, $3(Ca_3(PO_4)_2 \cdot CaF_2$ is an exceedingly insoluble compound. Fluorine in this combination would render insoluble eleven

times its weight of P_2O_5. Some correlation might indeed be indicated in Table 9 between the fluorine content and the P_2O_5 solubility after one month's storage at room temperature, if superphosphates 4 and 7 are eliminated. No correlation is apparent, however, in the ammoniated superphosphates that were subjected to longer storage and higher temperatures.

TABLE 8. CHEMICAL PROPERTIES OF VARIOUS COMMERCIAL SUPERPHOSPHATES
BEFORE AND AFTER AMMONIATION

Plant Location................... Superphosphate No...............	Va. 1	N. J. 2	Md. 3	N. Y. 4	La. 5	N. C. 6	Tenn. 7	N. J. 8
Analysis of Original Superphosphate								
% Moisture..............	4.5	7.7	5.9	7.6	8.3	4.5	6.5	7.2
% Free H_3PO_4...........	1.2	3.5	3.9	3.0	1.0	2.6	2.8	2.9
% Total P_2O_5...........	19.8	18.2	20.6	21.1	19.1	21.5	19.8	21.2
% C. I. P_2O_5............	0.39	0.20	0.28	0.45	0.48	0.13	0.48	0.41
% Available P_2O_5........	19.4	18.0	20.3	20.6	18.6	21.4	19.3	20.8
% of Total P_2O_5 available	98.0	98.9	98.6	97.9	97.5	99.4	97.6	98.1
% Fluorine..............	1.57	1.68	1.92	1.80	1.70	2.15	1.67	2.07
% $FePO_4$.................	1.10	1.14	1.16	1.81	0.80	0.91	2.10	1.06
% $AlPO_4$.................	2.77	1.55	1.99	2.36	1.98	1.43	4.33	1.57
% CaO..................	28.30	30.50	30.35	30.10	29.28	31.13	28.25	30.45
% SO_3..................	27.75	30.55	28.78	28.48	29.20	29.18	30.55	29.35
Mol ratio SO_3:CaO.......	0.685	0.701	0.664	0.665	0.698	0.655	0.759	0.674
Analysis of Superphosphate Ammoniated with Nitrogen Solution 2 at Ratio of 30 lb. Free NH_3/1000 lb. Superphosphate as Prepared								
% Total N..............	5.60*	4.56	4.59	4.57	5.26*	4.58	4.70	4.59
Wt. ratio free NH_3:Total P_2O_5								
Nominal..............	0.152	0.165	0.146	0.142	0.158	0.139	0.152	0.141
Found..............	0.216*	0.159	0.139	0.132	0.183*	0.128	0.148	0.137
% Total P_2O_5.............	17.3	16.4	18.5	18.5	17.1	19.2	17.1	19.2
% C. I. P_2O_5.............	0.36	0.27	0.40	0.79	0.32	0.24	0.51	0.61
% of total P_2O_5 reverted..	0.1	0.6	0.8	2.2	−0.6	0.7	0.6	1.7

* Original superphosphate contained some ammoniacal nitrogen.

Under severe storage conditions (80°C, 176°F) the three phosphates having the highest fluorine contents showed substantially lower reversion than the average of the group.

The citrate solubility of fluorapatite, unlike hydroxyapatite and tricalcium phosphate, shows little variation with changes in the citrate solvent[3] or with change in the proportion of sample weight to volume of citrate solutions used for the extraction[27, 29, 60]. The marked differences in results in Table 9 between the 0.5-gram and the 1-gram samples suggest that

TABLE 9. PERCENTAGE REVERSION OF TOTAL P_2O_5 IN AMMONIATED SUPERPHOSPHATES OF TABLE 8 AS AFFECTED BY TIME AND TEMPERATURE OF STORAGE AND BY FLUORIDE CONTENT

Super-phosphate No.*	% Fluorine	At Room Temperature for 36 Days,1 Gram Method	At 40°C				At 50°C				At 80°C		
			for 42 Days		for 124 Days		for 37 days		for 121 Days		for 27 Days	for 112 Days	
			1 Gram Method	0.5 Gram Method	1 Gram Method	0.5 Gram Method	1 Gram Method	0.5 Gram Method	1 Gram Method	0.5 Gram Method	1 Gram Method	1 Gram Method	0.5 Gram Method
1	1.57	1.1	4.1	0.8	6.6	1.0	5.2	1.5	7.6	2.6	7.7	12.6	5.8
7	1.67	3.5	6.9	3.3	9.2	5.1	8.1	5.2	10.1	7.0	12.0	20.3	9.3
2	1.68	1.5	5.4	0.9	9.3	3.1	6.6	2.0	9.6	3.8	9.1	14.7	7.3
5	1.70	1.1	4.2	0.6	8.8	0.4	5.6	0.4	9.6	1.5	16.8	26.1	8.3
4	1.80	3.3	7.5	4.5	9.9	5.1	8.1	4.6	9.9	6.5	12.0	21.8	11.1
3	1.92	2.1	4.9	2.3	5.9	2.4	4.9	2.8	6.5	3.3	7.0	11.0	7.3
8	2.07	3.1	5.9	2.5	8.7	3.4	7.2	3.1	8.6	4.0	9.1	13.7	5.3
6	2.15	4.5	7.4	3.1	8.7	3.2	8.4	3.8	9.8	5.8	8.9	11.7	5.6

* Arranged in ascending order of fluorine content.

fluorapatite formation was not a major factor in this reversion. Mixtures of pure chemicals simulating a 4–12–4 grade of fertilizer without dolomite developed no significant amounts of citrate-insoluble P_2O_5 even after ammoniation in the presence of fluorides at the rate of 50 pounds of ammonia per 1,000 pounds of superphosphate and storage in a moist condition for two weeks at 75°C (167°F)[17].

Vegetative tests[59] have indicated that additions of fluorides to an ammoniated mixture have little or no effect on the availability of its P_2O_5 content to plants.
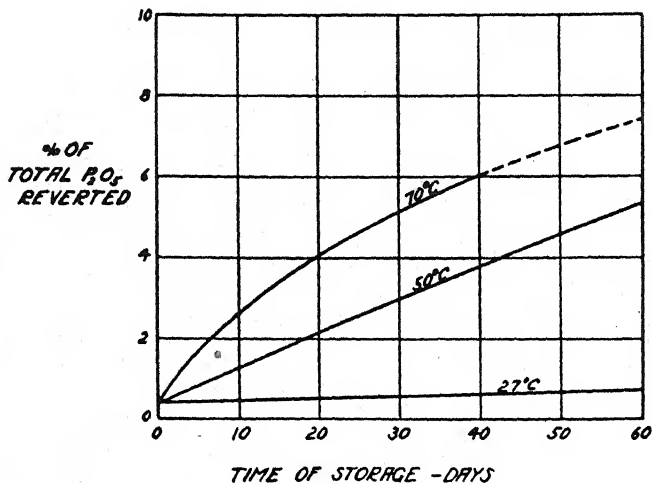
FIGURE 9. Effect of temperature and time of storage on the reversion of P_2O_5 in a 4-8-4 mixture (6% H_2O) ammoniated with nitrogen solution II at the rate of 30 lbs of free NH_3 per 1,000 lbs of superphosphate.

Effect of Moisture. Moisture has a significant influence on reversion. Figure 10 illustrates the effect in 4–8–4 mixtures that had been ammoniated with a solution which contained 60 per cent ammonium nitrate, 20 per cent ammonia, and 20 per cent water at the rate of 30 pounds of free ammonia per 1,000 pounds of superphosphate. The low reversion at ordinary temperature was not materially affected, but in 30 days' storage at elevated temperatures the reversion increased markedly with increasing moisture contents. At a low-moisture content (*e.g.*, 2 per cent) reversion was small even at elevated temperatures. The degree of ammoniation may be increased without excessive reversion provided that the moisture content is kept sufficiently low. Economy with respect to nitrogen may justify some expenditure for drying or even some sacrifice of available P_2O_5.

Effect of Neutralizing Additives. The growth in the consumption of physiologically neutral fertilizers has led to use of appreciable quantities of dolomite in ammoniated mixtures[24]. Calcic materials, such as high-calcium limestone, oyster shells, and marl, should not be used in ammoniated superphosphates because even at ordinary temperatures they cause reversion of available phosphate. Ground dolomite, $(CaCO_3 \cdot MgCO_3)$, however, may be used if excessive temperatures (above 45°C, or 113°F) are avoided.

Dolomite does induce change of the water-soluble P_2O_5 present as mono-
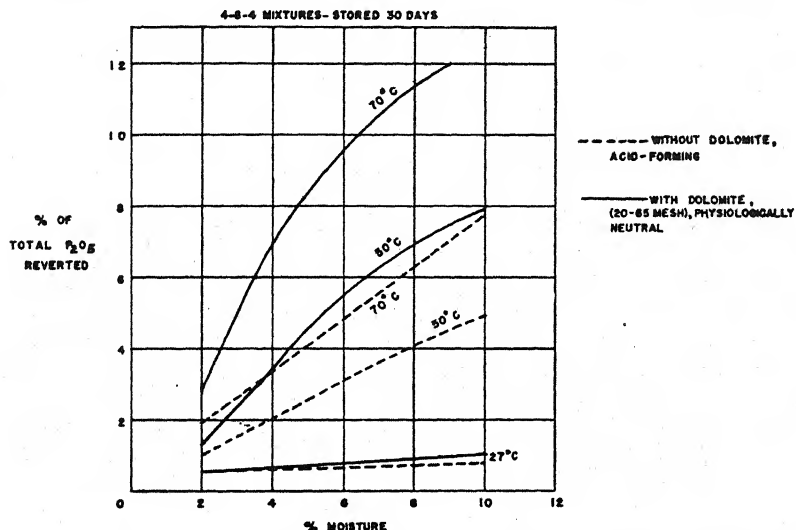
FIGURE 10. Effect of moisture and temperature on the reversion of P_2O_5 in a 4-8-4 mixture ammoniated with nitrogen solution II at the rate of 30 lbs of free NH_3 per 1000 lbs of superphosphate.

ammonium phosphate into dicalcium phosphate and magnesium ammonium phosphate, both of which are citrate-soluble[3, 34].

$$3NH_4H_2PO_4 + CaCO_3MgCO_3 \rightarrow CaHPO_4 + MgNH_4PO_4 + (NH_4)_2HPO_4$$
$$+ 2CO_2 + 2H_2O \qquad (9)$$
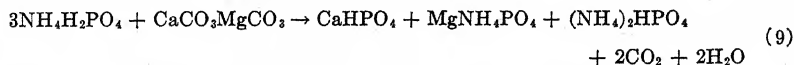
There is no loss in the availability of the P_2O_5 on standing at normal temperature. At elevated temperatures the diammonium phosphate which is formed in reaction (9) will decompose at significant rates, liberating ammonia, which in turn reacts in ammoniated superphosphate mixtures with the calcium sulfate and dicalcium phosphate to form ammonium sulfate and reverted phosphate:

$$(NH_4)_2HPO_4 \rightarrow NH_3 + NH_4H_2PO_4 \qquad (10)$$

$$2NH_3 + 2CaHPO_4 + CaSO_4 \rightarrow (NH_4)_2SO_4 + Ca_3(PO_4)_2 \qquad (11)$$
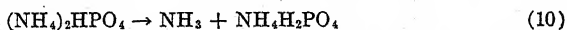
The over-all change in prolonged storage at elevated temperatures can be represented by the equation:

$$4NH_4H_2PO_4 + 2CaCO_3 \cdot MgCO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + 2MgNH_4PO_4 \qquad (12)$$
$$+ Ca_3(PO_4)_2 + 4CO_2 + 4H_2O$$
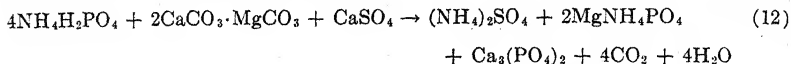
Storage of ammoniated superphosphate mixtures containing dolomite at temperatures over 45°C (113°F) for more than a few weeks leads to formation of considerable citrate-insoluble phosphate. Figure 10[31] gives reversion data for a 4–8–4 mixture without dolomite (acid-forming) and also for a comparable mixture made physiologically neutral with dolomite. In the normal range of moisture content, 4 to 10 per cent, the mixtures that contained dolomite suffered substantially higher reversions in 30 days' storage at elevated temperatures.

The formation of magnesium ammonium phosphate fixes a portion of the nitrogen in a slowly soluble form. Since ammonium sulfate and not diammonium phosphate results from reaction (12), no nitrogen is lost, even in 90 days' storage at 60°C (140°F)[9].

Greenhouse tests of mixtures which were ammoniated at the rate of 20 pounds of anhydrous ammonia per 1,000 pounds of superphosphate content and which were stored at ordinary temperatures with or without dolomite showed as good availability as the corresponding non-ammoniated mixtures[59]. The availability to plants of P_2O_5 in ammoniated mixtures containing dolomite became less if the proportion of ammonia exceeded 3 per cent of the superphosphate and if the storage temperature was above normal. Long-season crops gave favorable response to applications of mixtures containing dolomite, that had been treated with as much as 50 pounds of ammonia per 1,000 pounds of superphosphate, provided that the mixture had been stored at room temperature.

Physical Effects

The improvement in physical condition of superphosphate upon ammoniation may be attributed to evaporation of moisture, as a result of heating due to the chemical reactions, to the neutralization of the free acid, and to changes in the extent of hydration. Commercial superphosphates consist chiefly of monocalcium phosphate monohydrate, calcium sulfate predominantly in the form of anhydrite[43], and a somewhat syrupy solution of monocalcium phosphate in 30 to 60 per cent phosphoric acid. The water of crystallization in superphosphates appears not to change much upon ammoniation with anhydrous ammonia; there is tendency for an increase, but the differences are so small that x-ray methods failed to reveal them. If ammonia liquors are used the water of crystallization increases, especially upon aging. Changes in the amount of water of crystallization in ammonia-

tion come mainly from the decomposition of the hydrated monocalcium phosphate and the hydration of the calcium sulfate. The change in composition of the solution phase with ammoniation apparently is conducive to formation of $CaSO_4 \cdot \frac{1}{2}H_2O$ or $CaSO_4 \cdot 2H_2O$.

Ammoniation Solutions

The compositions and physical properties of the principal solutions used in the ammoniation of fertilizers are given in Table 10. Included for the purpose of comparison are anhydrous ammonia[51] and ammonia liquor[25]; solutions containing urea[23, 65] or ammonium nitrate[26, 46, 52] are used almost exclusively in current ammoniation practice.

Among the important factors in the selection of compositions for ammoniation solutions are the total nitrogen content, ratio of neutralizing nitrogen to total nitrogen, density, vapor pressure, salting-out temperature, physical properties of ammoniated products and relative costs of production. High total nitrogen content is advantageous in respect to storage and transportation costs. The amount of nitrogen that may be added commercially to superphosphate in the form of anhydrous ammonia or ammonia liquor is limited, since excessive additions cause reversion of the phosphates to insoluble forms. Hence low ratios of neutralizing ammonia to total nitrogen are generally desirable. Per unit of nitrogen present as neutralizing ammonia, Nitrogen Solution 4 and Urea Ammonia Liquor B supply respectively about 2.7 and 2.3 times as much total nitrogen as is supplied by ammonia liquor or anhydrous ammonia.

It is of practical importance that solutions containing high proportions of ammonium nitrate or urea are of relatively high density, that such a unit volume of solution contains almost as much nitrogen as an equal volume of anhydrous ammonia. For example, at 60°F the weights of product and of nitrogen contained in 10,000 gallons of the principal ammoniation liquids are:

Liquid	Tons Product per 10,000 gal at 60°F	Tons Nitrogen in 10,000 gal at 60°F
Anhydrous ammonia	25.7	21.16
Ammonia liquor, 30% NH_3	37.3	9.07
Nitrogen Solution 2A	47.6	19.32
Nitrogen Solution 3	45.0	18.36
Nitrogen Solution 4	49.3	18.25
Urea Ammonia Liquor A	41.0	18.67
Urea Ammonia Liquor B	43.6	19.71

The solutions should have low salting-out temperatures, otherwise precipitation of solids may cause troublesome plugging of valves and fittings

TABLE 10. COMPOSITION AND PROPERTIES OF AMMONIATING AGENTS

	NH_4NO_3 (%)	Urea (%)	NH_3 (%)	Ammonium Carbamate	H_2O (%)	Total N (%)	Nitrate N (%)	Urea N (%)	Inorganic N (%)	Ammonia N (%)	Approx. Sp. Gravity at 60°F	Approx. Vapor Pres. psi Gauge at 104°F	Approx. Temp. at which Salt Begins to Crystallize (0°F)	Equiv. Acidity, lb $CaCO_3$ Equiv. per Unit N	Equiv. Acidity, lb $CaCO_3$ Equiv. per 100 lb Product
Anhydrous ammonia	0.0	0.0	99.9	0.0	0.0	82.2	0.0	0.0	82.2	82.2	0.618	211		36	148
Ammonia liquor	0.0	0.0	30.0	0.0	70.0	24.6	0.0	0.0	24.6	24.6	0.895	11		36	44.6
Nitrogen sol. 2A	65.0	0.0	21.7	0.0	13.3	40.6	11.36	0.0	40.6	29.24	1.142	10	23	36	73.2
Nitrogen sol. 3	55.5	0.0	26.0	0.0	18.5	40.8	9.62	0.0	40.8	31.18	1.079	16	−13	36	73.5
Nitrogen sol. 4	66.8	0.0	16.6	0.0	16.6	37.0	11.65	0.0	37.0	25.35	1.182	1	48	36	66.6
Urea ammonia liquor A	0.0	32.5	28.9	18.1	20.5	45.5	0.0	15.1	30.4	30.4*	0.985	66	5	36	81.8
Urea ammonia liquor A diluted with 20 parts water per 100 parts liquor	0.0	27.1	24.1	15.1	33.7	37.9	0.0	12.6	25.3	25.3*	0.987	24	0	36	68.3
Urea ammonia liquor B	0.0	43.1	23.5	16.4	17.0	45.3	0.0	20.1	25.2	25.2*	1.046	55	30	36	82
Urea ammonia liquor B diluted with 20 parts water per 100 parts liquor	0.0	35.9	19.6	13.7	30.7	37.7	0.0	16.8	21.0	21.0*	1.038	24	30–35	36	68.4
Urea ammonia liquor 37†	0.0					37.1		9.1	20.6	20.6	1.05	25		36	67

* Includes NH_3 from ammonium carbamate.

† After ammoniation insoluble organic nitrogen compounds are formed which contain nitrogen equivalent to 7.4 per cent of the weight of the original liquor.

in cold weather, owing to crystallization in the supply lines. Relatively low ammonia and high solids contents are advantageous in warm weather because of the lower vapor pressures and smaller heats of ammoniation. For the ammoniation of fertilizer mixtures containing high proportions of alkaline materials like tobacco stems, a high solids content, as in Nitrogen Solution 4, is beneficial. Solutions rich in ammonia are preferred in very humid localities since goods ammoniated with solutions of high ammonium nitrate or urea content may cause difficulties due to hygroscopicity. Solutions of low-water contents naturally give drier products. The presence of small amounts of moisture in the superphosphate mixture is advantageous in respect to ease of absorption of ammonia in the mixture. Curing reactions also are facilitated. Drying of the ammoniated goods prior to storage may be desirable.

Important economies can be effected in the manufacture of ammoniation solutions since the expense of preparing solid ammonium nitrate or urea is obviated. Nitrogen solution 2A, for example, can be prepared by blending anhydrous ammonia with an 83 per cent aqueous ammonium nitrate solution obtained by neutralization of nitric acid with ammonia followed by partial evaporation through utilization of the heat of neutralization. This eliminates necessity for the costly process of evaporation beyond 83 per cent NH_4NO_3, and the expense of drying, packaging and handling the solid ammonium nitrate.

Urea-ammonia liquor may be marketed for ammoniation in substantially the form in which it comes from the synthesis autoclaves[12]. This eliminates the expense of distilling off the excess ammonia and carbon dioxide and of evaporating the resultant aqueous solution of urea to dryness[65].

Equipment For Ammoniation

The ammoniation of superphosphate, triple superphosphate, or mixtures is accomplished simply by spraying a measured weight[22, 36, 53] or volume of ammoniation solution, such as are listed in Table 10, into a weighed quantity of the solid materials. A diagrammatic sketch of the equipment is shown in Figure 11[5]. Chrome-iron or aluminum tanks and fittings give better life than ordinary steel parts in handling solutions containing ammonium nitrate[14]. Corrosion inhibitors are commonly used in the solutions[6].

To avoid salting-out in cold weather, the feed lines from the tank car to the measuring tank and the air line from the compressor to the tank may be insulated. Provisions should be made for ready cleansing of the lines. Instead of forcing the liquid to and from the storage tank with compressed air as indicated in Figure 11, centrifugal pumps have been used. Pumps sometimes give trouble due to vapor lock. If the packing glands of the pump are not tight, the leakage may be accompanied by evaporation

which causes the system to freeze up. The arrangement of valves, as shown in Figure 11, permits the discharge of the measuring tank by pressure and vent, dead-head pressure, or even by gravity.

The type of mixing equipment generally used for ammoniation is the 1- or 2-ton rotary batch mixer[2, 44] equipped with a distributor pipe near the axis of the mixer. In this machine the dry materials are lifted comparatively slowly by flights to the top of the rotary travel and then shower down to the bottom of the mixer to repeat the cycle. The 1-ton size affords 50 to 60 cubic feet of mixing space. Ammoniation solution to give 30 pounds of free ammonia per 1,000 pounds of run-of-pile superphosphate can be added in about 30 seconds[12, 57], if the mixer is in good repair, the closure
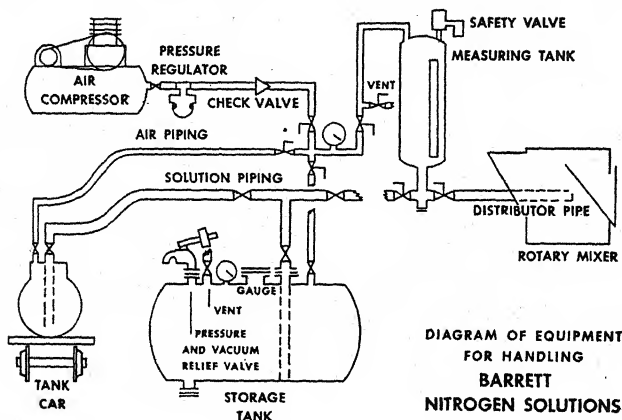
Figure 11.

fairly tight, and the solution well distributed. At 30 batches per hour this corresponds to absorption of 900 pounds of free ammonia by superphosphate in a mixing space of about 55 cubic feet, or an absorption rate of 16.4 pounds of NH_3 per cubic foot per hour. A coating of superphosphate builds up on the walls of the mixer and protects it from corrosion.

A pug-mill type ammoniator has been developed for continuous operation. The machine consists of a rugged steel tube having a central shaft on which are mounted strong steel blades set at a pitch to move the material forward in a violent state of agitation. The solution is sprayed through nozzles set in a recess along the top of the tube. In equipment of this type, having 13 cubic feet of mixing space, mixtures have been ammoniated at rates of 30 tons per hour at 28.6 pounds of ammonia per 1,000 pounds of superphosphate. This corresponds to absorption of 66 pounds of NH_3 per hour per cubic foot of mixing space.

Other types of equipment that may be applicable to continuous ammoniation are closed screw conveyors of rugged construction, and ribbon mixers. The uniform flow of materials that is required for the smooth operation of these continuous mixers has not always been realized.

Mixtures that are to be pelleted and subsequently dried require initial moisture contents up to 15 per cent. A pan mixer provided with means for introducing the solution below the surface of the mixture gives good absorption in these moist mixtures even when the degree of ammoniation is 45 to 65 pounds NH_3 per 1,000 pounds of superphosphate. The exposure of the mix facilitates evaporation of moisture. For uniform treatment in the drier, however, a continuous type of mixer is preferable.

Gravity-type mixers are also used for ammoniation. Further agitation can be provided by use of screw conveyors in handling the product discharged from the mixer.

Thorough dispersion of the ammoniation solution in the superphosphate is essential for good cure and to prevent undue reversion[21]. Although the volatilization of ammonia and moisture facilitates the distribution of the active reactants, and although reaction with the free phosphoric acid and monocalcium phosphate is very rapid, the reversion reactions are sufficiently rapid at high temperatures in the ammoniator to develop considerable insoluble phosphate within 2 minutes, in over-ammoniated portions of the charge. Prolonging the agitation does not remedy the damage to the over-ammoniated portions of the charge which have reverted to insoluble forms. The undesirable results of imperfect distribution persist as low availability in the over-ammoniated material and as poor physical characteristics in the under-ammoniated material.

Cooling. Ammoniated fertilizers as discharged from the mixer feel warm and somewhat moist; upon cooling, they become dry, friable, and under some conditions have desirable granular characteristics. If cooled to 38°C (100°F) or lower they can often be bagged and shipped within a few days. Material at temperatures above 45°C (113°F) should be cooled to avoid risk of reversion of the phosphates into insoluble forms in prolonged storage. At high degrees of ammoniation, temperatures at the mixer exit may range up to 102°C (216°F) though the usual range is from 54° to 66°C (130° to 150°F).

To cool ammoniated fertilizers before storage, overhead cranes may be used to move the warm fertilizer from one bin to another, the material being dropped from the maximum height to provide aeration. Some cooling takes place on belt conveyors. Rasping by dropping the product into a fan or cage-type disintegrator aerates the material as it is thrown through the air to the storage pile. The cooling effected in these ways is usually 5 to 6°C (8 to 10°F) at most, owing to inefficient contact with air, the small

volume of air, and the short time of exposure. Blowing air through an elevator used for conveying the product from the mixer to the storage pile gave in one test a temperature drop of 3.3°C (6°F)[19]. Cascading over flights supported by an open framework has also been done; in dropping 18 feet in 5 seconds fertilizer 61°C (110°F) above the ambient temperature cooled only 6.7°C (12°F)[19]. Although adequate cooling could be achieved in a pneumatic conveyor, the system has drawbacks in the handling of fertilizers.

A rotary cooler is an effective device for cooling ammoniated fertilizers[19]. The intimate contact of the fertilizer particles with the air and the temperature-moisture relationships in countercurrent cooling are such that 50 per cent of the heat can be removed by vaporization of moisture from the fertilizer. The relative temperature of the air is usually not so critical as its relative humidity. Normally between 4 and 7 cubic feet of air are required per pound of fertilizer. The optimum linear velocity of the air appears to be between 200 and 300 feet per minute. Engineering data indicate that 30 tons per hour can be cooled 22°C (40°F) in a rotary cooler 5 feet in diameter by 20 feet in length using 6 cubic feet of air per pound of fertilizer and vaporizing 0.5 per cent moisture. If the air-to-fertilizer ratio is not maintained above 5 cubic feet per pound in cold weather, condensation on the walls of the air ducts and cyclone dust collector may cause difficulty[18].

Economics

Anhydrous ammonia is now the lowest cost commercial form of fixed nitrogen. As pointed out in previous sections of this chapter, the quantity of uncombined ammonia that may be added to superphosphate commercially is limited by the possibility of excessive reversion of phosphate into insoluble forms when too much ammonia is added. It is usually not practicable to add to superphosphate more than 3 or 4 pounds of neutralizing ammonia per unit of water-soluble P_2O_5, corresponding to 2.5 to 3.3 per cent nitrogen in a 20 per cent superphosphate, although under certain favorable conditions greater amounts are sometimes employed.

By use of ammoniation solutions which contain highly soluble nitrogenous substances in addition to ammonia and water, it is practical to increase the proportion of nitrogen that is introduced in the ammoniation of superphosphate up to about 0.5 unit of nitrogen per unit of water-soluble P_2O_5. Ammonium nitrate and urea in solutions cost less to produce than the corresponding solids, because the necessity for expensive evaporation operations is eliminated. Many economies result from the use of solutions for ammoniation due to the higher nitrogen content of these carriers and the more rapid curing and easier handling of the resulting ammoniated prod-

ucts. The handling of nitrogen in liquid form reduces labor requirements. Use of ammoniation solutions of low vapor pressure instead of liquid anhydrous ammonia reduces cost of storage and handling facilities.

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18. Other Water-Soluble Phosphatic Fertilizers

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In addition to the water-soluble phosphatic fertilizers described in Chapters 15, 16 and 17, a number of products have been proposed, patented or developed on a commercial scale, involving the use of acids other than sulfuric and phosphoric. Moreover, several special types of fertilizers containing two or more of the basic plant-food ingredients (N, P_2O_5 and K_2O) have appeared on the market and are sold under trade names. Most of these latter products are intimate mixtures of compounds, but are so processed that each particle is virtually uniform in composition and hence danger of segregation of the various constituents is largely eliminated.

TREATMENT OF PHOSPHATE ROCK WITH OTHER ACIDS

Hydrochloric Acid

The decomposition of phosphate rock with hydrochloric acid has been suggested by Liebig[17], Horsford[13], Koefoed[16], Newberry and Barrett[22], Glaser[11], Pike[24], Seyfried[33], Fox and Whittaker[8, 10] and Fox and Clark[9]. It appears, however, that the manufacture of water-soluble phosphates suitable for fertilizer use by the direct treatment of phosphate rock with hydrochloric alone is commercially impracticable.

Although phosphate rock is readily decomposed by this acid, the product consists of a mixture of calcium chloride and either monocalcium phosphate or phosphoric acid (depending on the quantity of HCl used), together with dissolved fluorine compounds and other impurities. Disregarding the other rock components, these main reactions may be represented as follows:

$$Ca_3(PO_4)_2 + 4HCl \rightarrow CaH_4(PO_4)_2 + 2CaCl_2 \tag{1}$$

$$Ca_3(PO_4)_2 + 6HCl \rightarrow 2H_3PO_4 + 3CaCl_2 \tag{2}$$
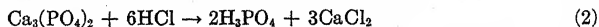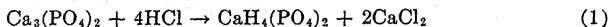
If the solution obtained according to equation (1) is evaporated, the product is a dense sticky mass entirely unfit for fertilizer use because of hygroscopic properties of the calcium chloride contained therein.

On the other hand, the separation of the calcium chloride is not possible

unless the acid solution is treated with lime, limestone or an alkali resulting in the precipitation of dicalcium phosphate as shown in equation (1).

$$CaH_4(PO_4)_2 + CaCl_2 + CaO \rightarrow 2CaHPO_4 + CaCl_2 + H_2O \qquad (3)$$
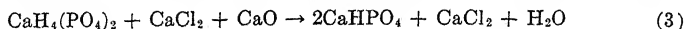
The precipitated dicalcium phosphate may then be filtered and washed free of soluble salts as described in Chapter 20. Whereas, the P_2O_5 in dicalcium phosphate is classed as available, it is not water-soluble and must be acidified to convert it into the latter form. Obviously, this is not economical in the case of fertilizers which are sold at a relatively low price.

Monocalcium Chlorophosphate

With a view to using low-cost by-product hydrochloric acid as an acidulating agent and obtaining a product that contains no free calcium chloride, Fox and Clark[9] proposed treating phosphate rock with a mixture of hydrochloric and phosphoric acid. On drying the resultant mass one-fourth of the hydrochloric acid is evolved for re-use and a compound known as monocalcium chlorophosphate is obtained which is no more hygroscopic than certain salts commonly used in fertilizers. The reactions involved may be represented as follows:

$$Ca_3(PO_4)_2 + 4HCl + H_3PO_4 + H_2O \rightarrow 3CaClH_2PO_4 \cdot H_2O + HCl$$
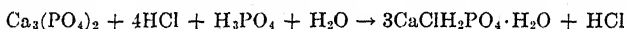
On heating this product to 225 to 300°C in the presence of steam it is converted into dicalcium phosphate with a further recovery of hydrochloric acid[2], as described in Chapter 19.

Crude monocalcium chlorophosphate prepared from phosphate rock, as outlined above, contains approximately 34 per cent of total P_2O_5 of which virtually all is water-soluble. Its concentration is about midway between ordinary superphosphate and triple superphosphate. So far this process has not been developed on a commercial scale. The specific gravity and strength of solutions of hydrochloric acid are given in Table 10 in the Appendix.

Nitric Acid

Processes for the treatment of phosphate rock with nitric acid and the nature and utilization of the products have been described and discussed by Schlutius[32], Braun[3], Bretteville[4], Foss[7], Hignett[100], Oehme and Hermuth[23], Quanquin[27], Plusjie[26] and Turrentine[35].

The treatment of phosphate rock with nitric acid appears offhand to offer the distinct advantage of utilizing the acid properties of this reagent to manufacture water-soluble fertilizers containing two plant-food ingredients (N and P_2O_5). Unfortunately, the physical nature of the products obtained is such that they are not well adapted for fertilizer use.

When phosphate rock and nitric acid are mixed in molecular proportions equivalent to those used in the manufacture of superphosphate by the

sulfuric acid process, the resultant product consists largely of a wet, highly soluble mixture of monocalcium phosphate and calcium nitrate. Disregarding the other components in the phosphate rock, the main reaction is shown in equation (4):

$$Ca_3(PO_4)_2 + 4HNO_3 \rightarrow CaH_4(PO_4)_2 + 2Ca(NO_3)_2 \qquad (4)$$
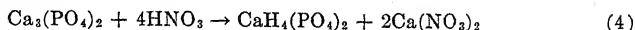
On heating this paste-like mixture to drive off the free moisture, approximately one-fourth of the nitric acid originally added is evolved, and the water-solubility of the P_2O_5 in the dried residue is greatly reduced due to the formation of dicalcium phosphate according to equation (5).

$$CaH_4(PO_4)_2 + 2Ca(NO_3)_2 \rightarrow 2CaHPO_4 + Ca(NO_3)_2 + 2HNO_3 \qquad (5)$$
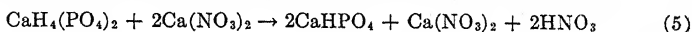
In addition to the lower solubility of the P_2O_5 in the dried product, the latter still contains sufficient calcium nitrate to give it objectionable hygroscopic properties.

The evolution of nitric acid on drying can be greatly reduced by ammoniating the mixture obtained in equation (4), but here again, the resultant product contains a very limited amount of water-soluble P_2O_5 and such high proportions of calcium and ammonium nitrates that it is very hygroscopic. The reaction of the material with ammonia may be represented by equation (6).

$$CaH_4(PO_4)_2 + 2Ca(NO_3)_2 + 2NH_3 \rightarrow 2CaHPO_4 + 2NH_4NO_3 + Ca(NO_3)_2 \quad (6)$$
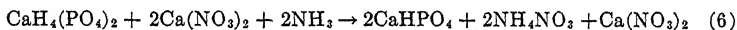
Whereas no completely water soluble phosphate product suitable for fertilizer purposes has yet been obtained directly by mixing finely ground phosphate rock with nitric acid alone, a number of processes have been proposed, patented or developed involving the use of this acid and the formation of products wherein the P_2O_5 is present chiefly as dicalcium or citrate-soluble phosphate. Some of these processes are designed to separate the dicalcium phosphate from the soluble nitrates that are simultaneously obtained, while others involve subsequent treatment whereby the nature of the products is changed to improve them for fertilizer use. Virtually all of these products contain substantial percentages of soluble salts other than phosphates.

A process and product described by Quanquin[27] is designed to overcome to a large extent the hygroscopic properties of the ammoniated product obtained according to equation (6). The process consists in adding sufficient potassium sulfate to the ammoniated product obtained according to equation (6) to react with the calcium nitrate, thus forming less hygroscopic potassium nitrate and calcium sulfate according to equation (7).

$$2CaHPO_4 + 2NH_4(NO_3)_2 + Ca(NO_3)_2 + K_2SO_4 \rightarrow 2CaHPO_4 + 2NH_4NO_3 + CaSO_4 + 2KNO_3 \qquad (7)$$
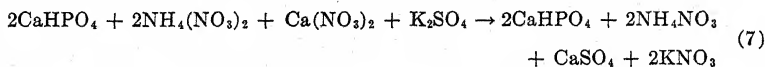
Such a product, however, still contains a sufficient quantity of ammonium nitrate to render it hygroscopic.

Another process similar to that proposed by Quanquin consists in mixing phosphate rock with nitric acid and ammonium sulfate. The reactions being represented thus:

$$
\left.
\begin{array}{l}
Ca_3(PO_4)_2 + 4\ HNO_3 + 3(NH_4)_2SO_4 \rightarrow \\
3\ CaSO_4 + 4\ NH_4NO_3 + 2(NH_4)H_2PO_4
\end{array}
\right\}
\tag{8}
$$
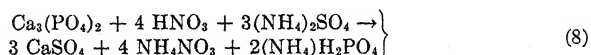
The precipitated calcium sulfate may be separated by filtration leaving a solution consisting of ammonium nitrate and monoammonium phosphate. Here again, however, the solution of mixed salts must be ammoniated before it is dried in order to prevent the evolution of nitric acid. The addition of ammonia converts a considerable portion of the P_2O_5 into dicalcium phosphate. One of the advantages claimed for this process is that the ammonium sulfate may be obtained without the use of sulfuric acid by reacting the separated calcium sulfate with ammonium carbonate as shown in equation (9)

$$
Ca\ SO_4 + (NH_4)_2CO_3 \rightarrow CaCO_3 + (NH_4)_2SO_4
\tag{9}
$$
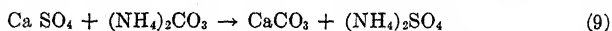
Another process covering the treatment of phosphate rock with an excess of nitric acid is practiced in Holland[6, 15] and comprises the crystallization and separation of the calcium nitrate $(Ca(NO_3) \cdot 4H_2O)$ obtained in equation (4) and ammoniating the mother liquor (containing the monocalcium phosphate) to produce a mixture of dicalcium phosphate and ammonium nitrate. This process involves crystallization, filtration and drying steps which render it somewhat questionable from an economic standpoint.

Some of these processes as well as those involving the use of mixtures of nitric acid with phosphoric and sulfuric acids, are being studied by the TVA with a view to working out the most practicable scheme for utilizing nitric acid as a reagent in the manufacture of fertilizer products.

Hignett[10a] considers the following four processes the most promising from an economic standpoint. (I) involves the treatment of phosphate rock with a mixture of nitric and phosphoric acids; (II) uses a mixture of nitric and sulfuric acids; and (III and IV) use nitric acid alone as an acidifying agent. In every case ammonia is added to neutralize or partially neutralize the acid solutions so that the bulk of the P_2O_5 in the final products is in the form of dicalcium phosphate.

(I)

$$
\left.
\begin{array}{l}
3\ Ca_3(PO_4)_2 + 14\ HNO_3 + 4H_3PO_4 \rightarrow \\
6\ H_3PO_4 + 7\ Ca(NO_3)_2 + 2\ CaH_4(PO_4)_2
\end{array}
\right\}
\tag{10}
$$

$$
\left.
\begin{array}{l}
6\ H_3PO_4 + 7\ Ca(NO_3)_2 + 2\ CaH_4(PO_4)_2 + 16\ NH_3 \rightarrow \\
9\ CaHPO_4 + 2(NH_4)HPO_4 + 14\ NH_4NO_3
\end{array}
\right\}
\tag{11}
$$

(II)

$$3\ Ca_3(PO_4)_2 + 10\ HNO_3 + 4\ H_2SO_4 \rightarrow \\ 6\ H_3PO_4 + 4\ CaSO_4 + 5\ Ca(NO_3)_2 \Big\} \tag{12}$$

$$6\ H_3PO_4 + 4\ CaSO_4 + 5\ Ca(NO_3)_2 + 11\ NH_3 \rightarrow \\ 5\ CaHPO_4 + (NH_4)H_2PO_4 + 4\ CaSO_4 + 10\ NH_4NO_3 \Big\} \tag{13}$$

(III)

$$Ca_3(PO_4)_2 + 6\ HNO_3 \rightarrow \\ 2\ H_3PO_4 + 3\ Ca(NO_3)_2 \Big\} \tag{14}$$

$$2\ H_3PO_4 + 3\ Ca(NO_3)_2 + K_2SO_4 + 4NH_3 \rightarrow \\ 2\ CaHPO_4 + 4\ NH_4NO_3 + 2\ KNO_3 + CaSO_4 \Big\} \tag{15}$$

(IV)

$$Ca_3(PO_4)_2 + 6\ HNO_3 \rightarrow \\ 2\ H_3PO_4 + 3\ Ca(NO_3)_2 \Big\} \tag{16}$$

$$2\ H_3PO_4 + 3\ Ca(NO_3) + 4NH_3 \rightarrow \\ 2\ CaHPO_4 + NH_4NO_3 + Ca(NO_3)_2 \Big\} \tag{17}$$

Separation of $CaHPO_4$ by filtration
$$Ca(NO_3)_2 + (NH_4)_2CO_3 \rightarrow \\ 2\ NH_4NO_3 + CaCO_3 \Big\} \tag{18}$$
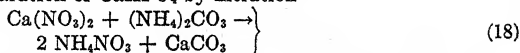
The expansion of the synthetic ammonia industry coupled with the fact that sulfuric acid is in short supply in many parts of the world, make it appear that processes for manufacturing phosphate fertilizers through the medium of nitric acid will receive increasing attention.

The specific gravity and concentration of solutions of nitric acid are given in Table 9 of the Appendix.

Hydrofluoric Acid

The treatment of phosphate rock with hydrofluoric acid presents some attractive possibilities. Its energetic chemical action toward silica and silicates would seem to make it ideal for enriching phosphates high in these impurities. Moreover, calcium fluoride, the product resulting from its reaction with certain lime compounds, is an insoluble substance which can be separated from the soluble ingredients by decantation or filtration.

On the other hand, hydrofluoric acid is not very effective in decomposing phosphates, due in part to the insoluble nature of the calcium fluoride which forms as a coating over the undecomposed phosphate, retarding or preventing further action by the acid. The fact also that hydrofluoric acid is chiefly derived from fluorspar (CaF_2), a relatively expensive raw material, and is much more valuable for other purposes, makes it appear rather unlikely that substantial quantities will ever be used in the production of fertilizer.

In the manufacture of superphosphate and triple superphosphate, how-
ever, both hydrofluoric and hydrofluosilicic acids are evolved. Gaseous
fluorine compounds, which may be collected as by-products, are also driven
off in preparing sintered or nodulized phosphate charges for subsequent
treatment in the electric or blast furnace, as well as in producing fused and
defluorinated phosphate rock.

Hechenbleikner[12] proposed to utilize these acids of fluorine to treat an-
other batch of phosphate rock and claimed that in dilute solutions they de-
composed the mineral phosphates very completely. He also stated that the
presence of gelatinous hydrofluosilicic acid in the dilute solution caused the
calcium fluoride precipitate to settle so rapidly and completely that the
phosphoric acid could be readily separated by decantation. He suggested
that this dilute phosphoric acid be used to reduce the concentration of
sulfuric acid to the proper strength for the manufacture of superphosphate,
thus enhancing the P_2O_5 content of the product.

Sulfur Dioxide (Sulfurous Acid)

Instead of being produced by the action of sulfuric acid on natural salts
or minerals, as is the case with the other so-called mineral acids, sulfur di-
oxide is obtained from the combustion of sulfur or pyrites and is the source
from which sulfuric acid itself is derived. The use of sulfur dioxide and sul-
furous acid to decompose phosphate rock has been proposed by Designolle[5],
Bergmann[1], Machalske[18], Meyers[21], Blumenberg[2], Sadtler[31]. If this general
scheme were feasible it would simplify the production of soluble or available
phosphates since the gases from burning sulfur or pyrites could be used
directly in treating phosphate rock instead of having to go through the
elaborate steps required in making sulfuric acid. Blumenberg[2], moreover,
claims that SO_2 does not attack the impurities of phosphate rock and hence
this method offers a means of handling phosphates unsuitable for treatment
with sulfuric acid. This claim does not appear to be supported by the facts.
Experience has been that the weak nature of sulfurous acid renders its action
upon phosphate rock very incomplete and, therefore, sulfur dioxide or sul-
furous acid alone is not an efficient reagent for decomposing mineral phos-
phates. Meyers[21], however, claims to overcome this objection by acting
upon the mineral (in the presence of water) with a mixture of SO_2, SO_3 and
air, and obtains such a mixture by passing the gases from burning sulfur or
pyrites through a catalyst before they come into contact with the phosphate
rock.

Hughes and Cameron[14] thoroughly investigated the possibilities of de-
composing phosphate rock with sulfur dioxide and sulfurous acid under
various conditions of temperature and pressure. Whereas they were able to
decompose phosphate rock with saturated aqueous solutions of sulfur di-

oxide at 25 to 100°C at pressures of from 3 to 10 atmospheres, the reactions are quite complex and accompanied by decomposition of some of the sulfur dioxide. These investigators concluded that no procedure in which sulfur dioxide was used as a reagent offered economic advantages over the standard method of manufacturing superphosphate.

PHOSPHAZOTE

Phosphazote is a fertilizer containing phosphoric acid and an organic nitrogen compound. This product was manufactured in France and Switzerland prior to World War II[29]. It is prepared by first treating a suspension of calcium cyanamid in water with carbon dioxide, resulting in the following reaction:

$$CaCN_2 + CO_2 + H_2O \rightarrow CaCO_3 + CN_2H_2 \tag{19}$$
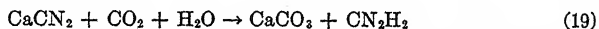
The calcium carbonate thus precipitated is filtered from the solution of free cyanamid and the latter treated with dilute sulfuric acid, carefully concentrated under reduced pressure and mixed with phosphate rock at a temperature of 60 to 70°C to yield a superphosphate of urea. Care must be exercised that the temperature does not rise above 70°C, otherwise the urea compounds will be partly converted into ammonium sulfate.

The dried product contains 15 per cent of P_2O_5 and 7 per cent N. Phosphazote is not a highly concentrated fertilizer and the cost of the several steps involved in its preparation renders the product of rather doubtful economic importance.

UREA PHOSPHATE

Urea phosphate $(CO(NH_3) \cdot H_3PO_4)$ is an addition product obtained by dissolving urea in 60 to 85 per cent phosphoric acid with the application of heat if necessary. The solution is then vigorously stirred while being cooled, seeded with a crystal of the salt, and the urea phosphate crystallized out. According to Ross and Merz[29], if the concentration of the phosphoric acid is approximately 85 per cent H_3PO_4, the entire mass solidifies into a product containing less than 10 per cent free moisture. Urea phosphate thus prepared approaches its theoretical composition (17.85 per cent N and 44.81 per cent P_2O_5) and contains a total of approximately 62.7 per cent of plant food. As in the case of phosphazote, however, a potash salt must be added to make up a complete fertilizer.

From the standpoint of concentration, urea phosphate has much to recommend it, but the product is hygroscopic, highly acid, and more expensive to manufacture than diammonium phosphate, which contains fully as much plant food.

NITROPHOSKA

The term nitrophoska is applied to a series of concentrated complete mixtures manufactured in Germany. All the mixtures in this group contain diammonium phosphate, ammonium nitrate, and potassium chloride or potassium sulfate. The total plant food content of the several grades of nitrophoska ranges from 50 to 60 per cent[19, 20, 29].

Nitrophoska is a partially reacted mass produced by adding a highly concentrated hot solution of ammonium nitrate to a mixture of the diammonium phosphate and a potash salt, and thoroughly stirring the mass until it forms granules on cooling. A partial base exchange takes place during the processing with the formation of a certain amount of potassium nitrate and ammonium chloride or sulfate, depending on which salt of potash is employed. Five grades of nitrophoska and their composition are given in Table 1.

TABLE 1. ANALYSIS AND FERTILIZER FORMULAS OF FIVE DIFFERENT GRADES OF NITROPHOSKA

Grade	Forms of Nitrogen		Analysis (%)			Fertilizer Formula (parts)			
	Ammon.	Nitrate	N	P_2O_5	K_2O	$(NH_4)_2HPO_4$	NH_4NO_3	KCl	K_2SO_4
I	11.3	6.2	17.5	13.0	22.0	24	35	35	
II	9.7	5.3	15.0	11.0	26.5	20	30	42	
III	11.5	5.0	16.5	16.5	21.5	31	29	34	
A	13.4	1.6	15.0	30.0	15.0	56	9	24	
C	10.8	4.7	15.5	15.5	19.5	29	27		36

The purpose of incorporating the hot solution of ammonium nitrate into the mixture of the other two ingredients and graining or granulating the mass is to reduce the hygroscopic properties of the final product. As far as known, very little nitrophoska has been manufactured in the United States. Although this product is less hygroscopic than ammonium nitrate alone, it tends to take up water and cake in a humid atmosphere, and hence is not too favorably regarded as an ingredient of complete fertilizers.

AMMOPHOSKA

Ammophoska is a term applied to a group of concentrates developed in the United States[20, 29]. These concentrates differ from the nitrophoskas in that they contain no ammonium nitrate; the nitrogen is present in the form of monoammonium phosphate and the potash as potassium sulfate. All the constituents of this series of concentrates have low hygroscopicities and appear to be well suited for the manufacture of complete fertilizers which can be stored and distributed without deterioration.

Ammophoska is made by mixing various proportions of ammophos (described in Chapter 17) with potassium sulfate. The composition of three grades of ammophoska and the proportions of the several compounds contained therein are given in Table 2.

The main disadvantage of ammophoska from an economic standpoint is that it involves the use of potassium sulfate, a relatively expensive potassium salt.

MONOPOTASSIUM PHOSPHATE

Turrentine[34] states that monopotassium phosphate may be manufactured by decomposing potassium chloride with phosphoric acid, thus driving off hydrochloric acid which is recovered as a by-product. He indicates that this is a relatively simple process that does not require an elevated temperature.

In actual practice, however, such a scheme has not proved to be commer-

TABLE 2. ANALYSIS AND FERTILIZER FORMULAS OF THREE GRADES OF AMMOPHOSKA

Grade	Analysis Formula (%)			Ingredients (parts)		
	N	P_2O_5	K_2O	$NH_4H_2PO_4$	$(NH_4)_2SO_4$	K_2SO_4
I	12	24	12	39	34	22
II	10	20	15	32	29	28
III	10	30	10	49	19	18

cially feasible unless an excess of phosphoric acid is employed and the mass heated to approximately 250°C. The product thus obtained is highly acid and in order to convert it into monopotassium phosphate, either potassium carbonate or hydroxide must be added to react with the free phosphoric acid. Since these latter potash compounds are relatively expensive, their use in the manufacture of fertilizers is not usually warranted.

Pike[7] suggests a somewhat different approach in the production of monopotassium phosphate. He proposes to fuse a mixture of potassium chloride and phosphoric and sulfuric acid in a rotary kiln at a temperature of 700°C, using much less acid than that required for monopotassium phosphate. Under these conditions it is claimed that the potassium chloride is completely decomposed and the chlorine evolved as HCl. While the material is still in the molten state, coal is added to reduce the sulfate present and drive off the sulfur as SO_2.

The product when cooled consists of a dark colored clinker from which an alkaline solution is obtained by leaching with water. The resulting solution, which is highly basic, is then treated with phosphoric acid until it shows a

pH of from 4.5 to 6 and when evaporated to dryness yields non-hygroscopic monopotassium phosphate.

Although very little monopotassium phosphate is yet available for agricultural use, this compound has excellent physical properties and is one of the most concentrated fertilizer salts[30].

MONOAMMONIUM AND MONOPOTASSIUM PHOSPHATES

An ingenious process for manufacturing a concentrate containing all three fertilizer ingredients (N, P_2O_5 and K_2O) was developed on a pilot plant scale by Ross[28, 29]. This process involves two main steps:

(1) Potassium chloride is digested with two or more equivalents of concentrated phosphoric acid at a temperature of 250°C, resulting in the formation of a mixture of monopotassium phosphate and phosphoric acid and the volatilization of hydrochloric acid, which is collected as a by-product.

(2) The thick slurry or solution of monopotassium phosphate and free phosphoric acid is diluted with water and ammonia passed into the solution until a thick slurry consisting of an intimate mixture of monopotassium and monoammonium phosphate is obtained.

The main reactions involved in these two steps are represented in equations (8) and (9):

$$KCl + 2H_3PO_4 \rightarrow KH_2PO_4 + H_3PO_4 + HCl \tag{20}$$

$$KH_2PO_4 + H_3PO_4 + NH_3 \rightarrow KH_2PO_4 + NH_4H_2PO_4 \tag{21}$$
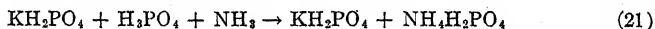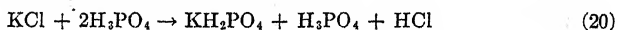
The product obtained when dried is a complete non-hygroscopic fertilizer having the following approximate composition:

$$
\begin{aligned}
N &= 5.6\% \\
P_2O_5 &= 56.5\% \\
K_2O &= 18.7\%
\end{aligned}
$$

Total plant food $= 80.8\%$

To insure the complete removal of chlorides as HCl, it is necessary that an excess of phosphoric acid be used in the decomposition of the KCl in the first step. The composition of the final product may be altered from that given above by varying the proportion of phosphoric acid used in the first step and the amount of ammonia passed into the solution in the second step.

This process has certain very attractive features, but its economic success depends to some extent on the utilization of the hydrochloric acid obtained as a by-product. If this latter acid is employed in the decomposition of a further quantity of phosphate rock, another plant must be constructed for the manufacture of dicalcium phosphate, and means provided for the disposal of large quantities of calcium chloride.

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19. Basic Slag, Degreased Bone and Dicalcium Phosphate

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AVAILABLE PHOSPHATES

Available Phosphates include a number of primary and secondary products resulting from the thermal and chemical treatment of the natural phosphates previously described. The term available, however, is a relative one and is applied to those phosphate carriers, the application of which experience has shown often result in additional crop yields, although the P_2O_5 which they contain is virtually insoluble in water.

The chemical nature of the phosphate compounds in some of these products is known, while in others the actual composition has not been accurately determined. Dicalcium phosphate and the metaphosphates of calcium and potassium are definite chemical compounds and certain highly basic phosphate crystals have been identified in basic slag. Calcined and fused phosphate rock consist presumably of tricalcium phosphate resulting from the elimination of fluorine from the apatite molecule, and the composition of degreased bone is fairly well-known.

On the other hand, available phosphates obtained by fusing phosphate rock with alkalies and alkaline-earth compounds may be solid solutions of rather indefinite composition, and complex but unidentified compounds no doubt occur in certain organic wastes and by-products.

While attempts have been made to measure the availability of such phosphates by their solubility in certain weak acids and dilute solutions, no laboratory method has yet been devised which will accurately determine the rate at which these phosphates dissolve in the soil solution or give a true index of their effectiveness under soil conditions. The laboratory tests for the availability of phosphates therefore are largely empirical, having been built up or evolved by ascertaining what media will dissolve those types of phosphates which have been found effective in field practice. Nevertheless, experience has shown that these tests at least give useful indications of the availability of such phosphates under soil conditions.

The American Association of Official Agricultural Chemists recognizes as

available all the P_2O_5 which is dissolved from a specified weight (1.0 gram) of the sample by a definite volume (100 cc) of a neutral solution of ammonium citrate; in the case of basic slag, European countries employ the so-called Wagner method which classes as available the P_2O_5 dissolved by a definite volume of a 2 per cent citric acid solution.* These methods of determining the availability of phosphates are described in Appendix VIII.

Several plausible arguments are offered in favor of the sparingly soluble phosphates over those that dissolve readily in water. The fact that plants draw their sustenance from a soil solution that is relatively dilute with respect to plant nutrients indicates that highly soluble fertilizers may be neither necessary nor desirable. Moreover, there is evidence that water-soluble phosphates react with certain soil constituents (Al_2O_3 and Fe_2O_3) very soon after they have been applied, forming compounds that are much less soluble than those phosphates that are classed as available (but not water-soluble). It is claimed also that the sparingly soluble phosphates release P_2O_5 at a rate more nearly conforming to that at which the plant can utilize it and hence a more or less constant concentration of the soil solution is maintained.

The following products and by-products which are are insoluble or very sparingly soluble in water are generally recognized as available to plants under favorable soil conditions:

        (1) Basic slag.
        (2) Steamed and degreased bone.
        (3) Dicalcium phosphate.
        (4) Calcium and potassium metaphosphates.
        (5) Defluorinated and fused phosphates.

MANUFACTURE AND PROPERTIES OF BASIC SLAG

Basic slag obtained as a by-product in the manufacture of steel by either the basic Bessemer or the basic open-hearth process is by far the greatest source of so-called available P_2O_5 for fertilizer purposes. This product, however, is used much more extensively in Europe than in this country. The consumption of basic slag as a phosphate fertilizer is second only to that of superphosphate, and during both World Wars certain countries had to depend largely on this material to meet agricultural demands for phosphoric acid. Prior to World War II, basic slag supplied about 70 per cent of the P_2O_5 used for fertilizer purposes in Germany and a substantial proportion of that used in France, Belgium and England. The production of basic slag in the more important European countries from 1935 to 1938 is given in Table 1. Statistics during the war period are not available.

* The Wagner method is no longer official in the United States.

Basic slag was first produced in efforts to handle highly phosphatic iron ores which were formerly considered unfit for smelting purposes because of the deleterious effect of phosphorus upon steel to be used for structural purposes or submitted to heavy strains. In 1878, however, two Englishmen, Thomas and Gilchrist, worked out a process for completely removing this element from pig iron so that high-grade steel could be manufactured from these phosphatic ores. Seven or eight years later it was found that the basic

TABLE 1. PRODUCTION OF BASIC SLAG BY COUNTRIES, IN METRIC TONS[1]

Country	1935	1936	1937	1938
Europe				
Belgium[2]	569,000	605,000	825,000	857,000
Czechoslovakia	125,000	145,000	162,562	162,000
Eire	—	1,250	1,481	1,682
France	940,000	1,035,000	1,218,000	860,000
Germany	2,025,000	2,277,000	2,312,000	2,550,000
Italy	1,731	1,113	840	([3])
Luxemburg	396,000	431,076	532,458	319,600
Poland	1,000	([3])	5,000[4]	8,100
Sweden	15,000	15,713	15,442	([3])
U. S. S. R.	41,000	([3])	([3])	([3])
United Kingdom[4]	276,000	302,000	410,000	471,000
	4,389,731	4,813,152[5]	5,481,783[6]	([3])
North America: United States[2]	25,000	35,600	35,600	35,600
	4,414,731	4,848,752	5,517,383	5,264,900

[1] Adapted from figures as published by Imperial Institute, London.
[2] Estimated.
[3] Data not available.
[4] Estimated amount ground and used as fertilizers.
[5] Exclusive of Poland and U. S. S. R.
[6] Exclusive of U. S. S. R.

slag obtained as a by-product in this process was an excellent phosphatic fertilizer.

Phosphorus is present in pig iron as iron phosphide (Fe_3P) and its removal can only be effected by oxidation at high temperatures in the presence of basic materials having a strong affinity for the resultant P_2O_5.

Since iron phosphide is not appreciably attacked until the silicon, carbon and manganese present in the iron are oxidized, these impurities must be removed from the molten metal before the phosphorus is burned.

The reactions involved and the products formed in the removal of phosphorus from pig iron are rather complex but may be represented as follows:

$$2Fe_3P \quad +6O_2 \quad \rightarrow 4FeO \quad + Fe_2O_3 + P_2O_5 \tag{1}$$

Iron   Air or   Ferrous   Ferric   Phosphorus
Phosphide   Oxygen   Oxide   Oxide   Pentoxide

$$P_2O_5 \qquad + 4CaO \rightarrow Ca_4P_2O_9 \tag{2}$$

Phosphorus   Lime   Tetracalcium
Pentoxide   Phosphate
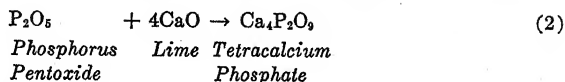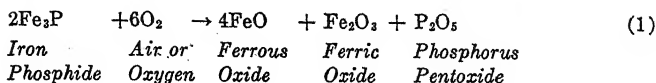
In any event the final compounds of phosphorus are contained in a slag which has proved to be a highly effective fertilizer material.

Basic Bessemer Slag

The equipment used in the basic Bessemer process consists of a pear-shaped steel vessel (known as a convertor) open at the top and provided with a number of inlets in its bottom for the introduction of air under heavy pressure. This vessel may be tilted on a horizontal axis to allow for the introduction of the molten iron and for pouring the slag and steel produced. It is lined with suitable basic materials (dolomite and limestone) which have a strong affinity for phosphoric acid (P_2O_5) and which form a molten slag with the oxidized silicon and other impurities contained in the metal.

In actual operation the molten iron high in phosphorus is poured into this convertor at a temperature of about 1,200°C, and a heavy blast of preheated air blown up through the metal. The temperature of the mass rises rapidly to above 1,800°C, due to oxidation of the silicon, manganese, carbon and phosphorus which burn with characteristic flames in the order named. The phosphorus is oxidized to P_2O_5, which in turn is seized by the basic lining of the vessel and converted into complex phosphates. When the "blow," determined by the character of the flame, is completed, the convertor is tilted, the air blast turned off, and the highly phosphatic slag which floats on the molten steel is run into a slag pot or ladle (to which is added also certain quantities of finely pulverized silica). The slag is then either dumped immediately and its temperature rapidly reduced or it is allowed to cool slowly in the ladle and is removed in a single lump, which is broken into fragments by repeatedly dropping a heavy steel ball (attached to a chain) upon the mass. The fragments are passed over a magnetic separator to remove entrapped steel particles and then fed to a ball mill wherein it is ground so at least 80 per cent will pass a 100-mesh screen.

There is considerable difference of opinion as to the effect of rate of cooling on the chemical and physical properties of basic slag. Gray[8] states that it is much harder to grind slag which has been allowed to remain in the ladle and that it should be removed and disintegrated as soon as it can be readily handled. Fritsch[7] states that poured basic slag if cooled quickly, is difficult to grind. Crowther[5] claims that basic slag cooled from its melting

point (1,700°C) to 1,100°C and held for some time at the latter temperature, loses much of its solubility, due probably to the formation of hydroxyapatite $(Ca_5(PO_4)_3OH)$.

According to Kaysser[13] the availability of the P_2O_5 in basic slag is increased by rapid cooling. Chirokov[4] claims that quenching the slag with water not only disintegrates it, but also increases its solubility. This latter practice however is fraught with some risk because of the steel entrained in the slag which is apt to cause an explosion. Both Gray[8] and Fritsch[7] say that where the ratio of Fe_2O_3 to FeO is about 1 to 3, the product is more readily ground than where the proportion of FeO is higher.

Basic Bessemer slag when finely ground is a dense product having a specific gravity ranging from 3 to 3.5. It varies in color from dark gray to almost black depending upon the quantities and proportions of the several

TABLE 2. COMPOSITION OF BASIC BESSEMER SLAGS
(According to Mayer)

Constituent	Composition (%)
P_2O_5	11.0 to 23.0
SiO_2	3.0 to 13.0
CaO	38.0 to 59.0
Fe_2O_3	6.0 to 25.0
MnO_2	1.0 to 6.0
Al_2O_3	0.2 to 3.7
MgO	2.0 to 8.0
S	0.2 to 11.4

ingredients contained therein and how they are combined. In addition to the P_2O_5 present, basic slag is valued for its content of lime and magnesia which play important roles as soil conditioners.

According to Mayer[16] the composition of basic Bessemer slag falls within the limits given in Table 2.

While it is highly essential that the silica content of the slag should be kept down during the blow in order to insure the complete elimination of the phosphorus from the steel, it has been found that in slags of equal P_2O_5 content those having the higher percentage of silica usually show a great availability both by laboratory and field tests. It is therefore customary to add silica to the molten slag when it is poured from the convertor[8] and Wagner[21] states that the availability of the P_2O_5 is thus increased from 10 to 30 per cent.

The effective fertilizer ingredient in basic slag is generally believed to be tetracalcium phosphate $(Ca_4P_2O_9)$ and the presence of this compound has been determined by a number of investigators[7, 9, 23]. The mineral "Isokla-

site" $(Ca_3P_2O_8 \cdot Ca(OH)_2 \cdot 4H_2O)$ which is found with hornstone or brown spar is the nearest approach to tetracalcium phosphate occurring in nature[6].

By no means all of the phosphoric acid present in basic slag is combined as tetracalcium phosphate for other crystalline compounds containing P_2O_5 combined with lime and silica have been identified[3, 9, 14, 20].

Kroll[14] gives the following list of compounds which have been determined present in basic slag:

Silico-carnotite	$3CaO \cdot P_2O_5 : 2CaO \cdot SiO_2$
Hilgenstockite	$4CaO \cdot P_2O_5$
Steadite	$3(3CaO \cdot P_2O_5) : 2CaO : 2CaO \cdot SiO_2$
Thomasite	$6CaO \cdot P_2O_5 : 2FeO \cdot SiO_2$

The first of these silico phosphates was later prepared synthetically and found to be very much more soluble in 2 per cent citric acid than tetracalcium phosphate.

Wagner believed that the P_2O_5 in basic slag is in the form of a double salt of calcium phosphate and calcium silicate and that probably some of the P_2O_5 is united with iron as basic iron phosphate. Cameron and Bell[2] state that the efficiency of basic slag seems to depend chiefly on the degree of fineness to which it is ground and that the tetracalcium phosphate it contains is probably unstable in aqueous solutions. According to Russell[18] it is generally believed in Great Britain that the P_2O_5 in basic slag is combined as a silico-phosphate which is assumed to have a different physiological action in the soil than the ordinary mineral phosphates.

Whatever the compounds of phosphorus may be in basic slag (free from fluorine), carefully controlled pot and field experiments have shown that the P_2O_5 contained therein is readily available under soil conditions.

When basic slag was first placed upon the market it was customary to sell it on the basis of its total P_2O_5 content and the degree of fineness to which it was ground. These specifications, however, led to the adulteration of basic slag with finely ground phosphate rock which necessitated devising some method by which a mixture of the two materials might be identified. For this purpose Wagner[22] proposed a mixture of dilute ammonium citrate and free citric acid. Later, in September, 1896, the Union of German Experiment Stations at Kiel adopted the 2 per cent citric acid test and did away with the total P_2O_5 standard and fineness of product after checking the solubility of P_2O_5 in this medium with the results obtained by pot experiments. In Table 3, given by Lindsey[15], it will be seen that in the majority of cases results obtained by these two methods checked fairly closely.

Basic slag is also soluble in carbonated waters and in Table 4 the results obtained by Reis and Arens show the relative solubility of several slags and various other phosphate-bearing materials in water saturated with CO_2. It

will be noted that in most instances the P_2O_5 in the slags has a much higher solubility than that in bone, phosphorite or even dicalcium phosphate.

TABLE 3. RELATION BETWEEN THE SOLUBILITY OF THE P_2O_5 OF BASIC SLAG IN 2 PER CENT CITRIC ACID AND ITS AVAILABILITY AS SHOWN BY POT EXPERIMENTS

Brand of Slag	Availability of P_2O_5	
Number	In 2 per cent acid	In pot tests
1	100	100
2	85	80
3	81	72
4	72	72
5	73	66
6	76	63
7	39	40
8	48	38
9	42	38
10	45	31
11	38	30

TABLE 4. SOLUBILITY OF BASIC SLAG IN WATER SATURATED WITH CARBONIC ACID

	Content of			Quantities Dissolved by 10 Liters of Water Saturated by CO_2			Comparative Solubility		
	SiO_2 (%)	P_2O_5 (%)	CaO (%)	SiO_2 (%)	P_2O_5 (%)	CaO (%)	SiO_2 (%)	P_2O_5 (%)	CaO (%)
Basic slag I	2.57	18.30	48.68	1.51	4.19	19.37	58.8	22.9	39.8
Basic slag II	5.20	15.07	48.82	3.15	5.66	24.84	50.9	37.4	51.0
Basic slag III	2.85	21.30	48.36	2.11	7.55	27.85	74.0	35.5	57.5
Basic slag IV	4.05	18.33	50.35	2.27	6.81	24.19	56.0	37.5	48.0
Basic slag V	7.67	16.32	47.98	4.22	7.89	24.54	56.3	48.1	51.1
Basic slag VI	6.93	15.74	48.15	3.55	4.50	25.08	51.2	28.7	52.0
Basic slag VII	5.54	24.00	46.35	3.05	7.59	19.36	86.1	31.6	41.7
Shell slag	18.15	13.47	44.10	4.99	3.45	15.17	27.4	25.5	34.4
Prepared slag	6.58	24.95	51.25	4.07	7.79	21.00	61.8	31.2	40.9
Scheibler's precipitate	8.02	33.36	31.10	0.62	7.36	9.37	7.7	22.0	30.1
Hoyermann's precipitate	5.70	14.93	34.05	1.29	4.96	19.96	22.7	33.0	58.5
Dicalcic phosphate of lime		51.09	41.03		8.57	6.95		16.8	16.8
Tricalcic phosphate of lime		43.26	51.45		5.41	7.04		12.5	13.6
Tetracalcic phosphate of lime		36.85	62.70		15.52	33.27		42.1	53.0
Degreased cattle bones		25.23	32.75		7.19	9.65		28.5	28.9
Bone ash made from above bones		41.71	55.75		2.29	3.29		5.5	5.9
Phosphorite	1.77	32.00	45.36	0.10	1.00	1.67	5.7	3.1	3.8

Basic Open-Hearth Slag

Open hearth furnaces are adapted to produce steel in much greater quantities than Bessemer convertors and where the character of the iron permits, are more widely employed. These furnaces are of two general types, namely, fixed or stationary furnaces from which slag and steel are periodically tapped through notches provided for this purpose and tilting furnaces which permit the pouring of the molten charge.

In the basic open hearth method iron ore and lime are charged upon the
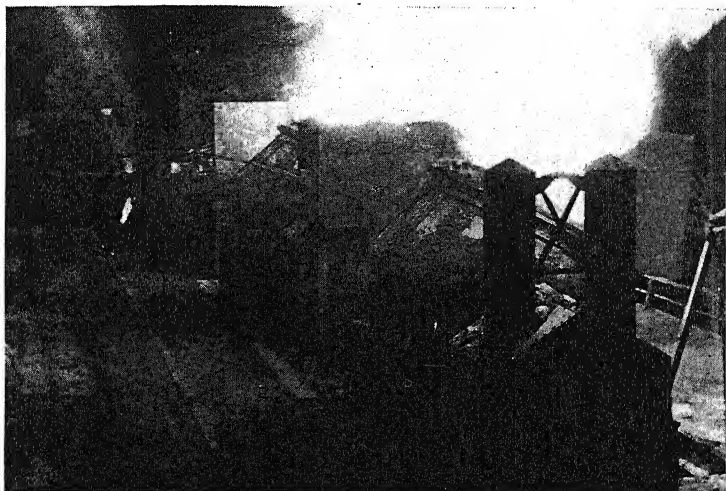
(Courtesy of Tennessee Coal, Iron and RR Company)

FIGURE 1. Two Bessemer converters in operation. In the basic Bessemer process, these converters are lined with limestone and dolomite which combines with the P_2O_5 produced when air under pressure is blown through the high-phosphorus molten iron.

hearth of an arched chamber or furnace heated by oil or producer gas, and the molten iron poured over these heated materials. A basic slag containing phosphoric acid and most of the other impurities is thus formed and tapped or poured from the furnace when the metal has reached the proper degree of purity.

The basic open hearth process may be divided into the "cold metal" and "hot metal" modifications. In the former a large proportion of steel scrap is used and hence the slag obtained is relatively low grade; in the hot metal modification the steel is largely derived from pig iron containing an appreciable percentage of phosphorus and hence the resultant slag is usually richer in P_2O_5.

The main distinctions between the basic Bessemer and basic open hearth processes are that in the former process the oxygen necessary for the purification of the metal is derived entirely from the air which is blown through the molten mass and the high temperature required is obtained from the combustion of the silicon, carbon and phosphorus contained in the metal. When using this process, therefore, a pig iron rich in phosphorus is actually desirable in order to insure the necessary high temperature.

In the basic open-hearth process on the other hand, 70 per cent of the oxygen required for the purification of the metal is derived from the iron ore charged to the furnace, and only 30 per cent from the oxidizing gases in the furnace. Moreover, the heat necessary for the reactions is largely supplied from an outside source. The manufacturer of open hearth steel prefers to use a low phosphorus pig iron and this fact, coupled with the greater proportion of slag produced, makes the phosphate content of basic open-hearth slag considerably lower than that of basic Bessemer slag. Russell[18] states that there are three distinct furnace products used for agricultural purposes in England under the name of basic slag: (1) high-grade basic Bessemer slag containing 20 per cent of P_2O_5 (85 per cent citric soluble); (2) open-hearth basic slag containing from 7 to 14 per cent P_2O_5 (85 per cent citric-soluble); (3) open-hearth basic slag containing from 7 to 10 per cent total P_2O_5 (only 20 per cent of which is citric-soluble) in the manufacture of which considerable quantities of fluorspar (CaF_2) have been employed as a flux.

Approximately thirty years ago it was found that the addition of fluorspar to the charge in the open-hearth furnace increased the fluidity of the slag and speeded up the steel-making process. This is particularly true in the manufacture of high-carbon steels (0.5 to 0.85°C).

Unfortunately, the addition of fluorspar greatly diminishes the solubility of the P_2O_5 in the slag and its efficiency as a fertilizer. This is due to the formation of fluorapatite or complex compounds having the apatite structure which are notably insoluble in both ammonium citrate and citric acid solutions[20].

The chief aim of the steel manufacturer, however, is to produce metal at the lowest possible cost, and in some cases the addition of fluorspar saves considerable time, labor and fuel, thus more than offsetting the reduction in the value of the resultant slag.

Consequently, much of the basic open-hearth slag has been materially decreased in value because of the fluorspar employed for fluxing purposes. According to Gray[3] some steel works employing the basic open-hearth process pay particular attention to the production of high quality slag. In such plants, it is the practice to draw off the bulk of the slag through a notch before the addition of fluorspar. This scheme is particularly adapted to open-hearth furnaces of the tilting type.

Basic slag rich in P_2O_5 cannot be produced where high carbon steel is required since carbon oxidizes before the phosphorus. Therefore, low phosphorus pig iron must be used in the open-hearth furnace where steel of this type is manufactured.

Processes for the Enrichment of Basic Slag

Various schemes have been proposed for the enrichment of basic slag to increase its agricultural efficiency and hence its sales value. Most of these processes have certain objectionable features and few have proved economical when tried on a commercial scale. Brief discussions of some of these processes appear warranted to acquaint the reader with the problems involved in raising the P_2O_5 content of basic slag.

Addition of Phosphate Rock to Molten Slag. It has been suggested that finely ground phosphate rock be added to the molten slag as it is tapped from the furnace, on the assumption that the slag will react with this mineral and convert the insoluble P_2O_5 contained therein to an available or citric acid-soluble form[11, 17]. This scheme has proved to be neither practical nor effective for the following reasons:

(1) It is difficult to distribute the finely ground rock throughout the mass of slag, or cause it to dissolve therein; hence merely increasing the total P_2O_5 content of the slag without increasing the quantity of available P_2O_5 is of no advantage.

(2) Even if the phosphate rock can be made to react with the molten slag by subsequent mixing or stirring, the amount of soluble P_2O_5 in the final product is apt to be less than it was before treatment[5]. This has been proved by Jacob and his co-workers[11] studying the role of small quantities of fluorine in reducing the solubility of phosphates of lime.

This latter objection applies also to the introduction of phosphate rock directly into either the basic Bessemer or open-hearth furnace[10, 16], since in the presence of basic materials the fluorine is largely retained by the slag and adversely affects the solubility of the P_2O_5.

Addition of Phosphate Rock to the Blast Furnace. The addition of phosphate rock along with iron ore and limestone directly into the blast furnace was suggested by Mehner in 1910, and a similar scheme for the manufacture of ferro-phosphorus was applied commercially for a number of years in the Tennessee phosphate fields. Such a practice raises the phosphorus content of the pig iron and the fluorine is discharged in the blast furnace slag.

On bessemerizing or treating this high phosphorus pig in the basic open-hearth furnace, slags can be produced which have a higher content of available or citric acid-soluble P_2O_5 than those derived from low phosphorus pig.

On the other hand, more time is required in the steel making step in order to reduce the phosphorus content of the metal to the desired point. Moreover, since the production of metal low in phosphorus is the primary

objective, it is difficult to persuade the steel maker to add further quantities of this objectionable impurity to the furnace stock.

Bertrand-Theil Process

Jones[12] has somewhat hesitantly suggested the use of the Bertrand-Theil process for enriching basic slag and describes this method as follows:

"In this process which is a modification of the open hearth process, two furnaces are used in place of one. In the primary furnace pig iron without scrap is worked with a highly basic slag. Simultaneously, scrap, oxide of iron and limestone are heated to a high temperature in the secondary furnace. When practically all of the silicon and phosphorus have been removed in the primary furnace the metal is transferred to the secondary furnace, where the process is completed. As no scrap is used in the primary furnace, the slag is not diluted thereby, and a grade containing a high percentage of phosphorus can be obtained in this way. The bulk of the phosphorus having been eliminated in the primary furnace the slag in the secondary furnace is necessarily low in phosphoric acid."

Duplex Process

The amorphous red hematite ores of Alabama are appreciably higher in phosphorus than the ores from which most of the iron and steel produced in the United States are derived.

A typical analysis of this Alabama ore as given by Bowran[1] is as follows:

ANALYSIS OF TYPICAL BIRMINGHAM IRON ORE

	(%)
Moisture	1.00
Iron (Fe)	36.31
Silica (SiO_2)	16.82
Alumina (Al_2O_3)	3.20
Lime (CaO)	14.22
Manganese (Mn)	0.17
Phosphorus (P)	0.35

Pig iron produced from this ore has the following analysis:

ANALYSIS OF PIG IRON PRODUCED FROM BIRMINGHAM ORES

	(%)
Silicon (Si)	0.70 to 1.00
Sulfur (S)	0.075 max.
Phosphorus (P)	0.80 to 1.00
Manganese (Mn)	0.35 to 0.45
Fe	97.50 to 99.08

Pig iron of the above composition is first treated in an acid Bessemer convertor to remove the silicon, carbon and manganese and the resultant metal (high in phosphorus) separated from the siliceous slag by pouring off

the latter. The blown metal enriched in phosphorus is then added to the basic open-hearth furnace and is washed through the molten basic slag. The phosphorus is thus oxidized, and the resultant P_2O_5 combines with the lime of the slag to form basic phosphates. According to Bowran[1] the ferrous oxide content of the slag can be so controlled that it is unnecessary to add any fluorspar to the open-hearth slag to promote fluidity and hence the P_2O_5 in the slag is highly available as a fertilizer.

A typical analysis of this slag, kindly furnished the writer by Mr. B. P. Curtis of the Tennessee Coal Iron and R. R. Company which manufactures a substantial tonnage of this product, is given below.

ANALYSIS OF BASIC SLAG PRODUCED BY DUPLEX PROCESS FROM ALABAMA PIG IRON

	(%)
Iron oxide (FeO)	9.62
Iron oxide (Fe_2O_3)	15.34
Silica (SiO_2)	10.72
Alumina (Al_2O_3)	1.63
Lime (CaO)	40.88
Magnesia (MgO)	5.44
Manganese oxide (MnO)	2.98
Total Phosphoric Acid (P_2O_5)	10.81
Citric acid Sol. (P_2O_5)	8.89
Carbon dioxide (CO_2)	1.68
Arsenic (As)	0.008
Copper (CU)	.004
Fluorine (F)	.150

The slag is poured from the tilting open-hearth furnaces into slag boxes and as soon as it has cooled to a point where it can be handled, the cakes are broken up by dropping a 5-ton steel ball on them. Most of the steel entrained in the slag is removed by a magnetic separator after which the product is taken up by a grab bucket, crushed to a size of $1\frac{1}{2}$ inches and ground in a ball mill to a fineness of 90 per cent through a 100-mesh screen. This product is sold as a soil conditioner.

The use of basic slag in American agriculture is rather limited, and most of that which is consumed is imported. This is not due to lack of appreciation of the merits of this product but to the fact that the bulk of the domestic iron ores are so low in phosphorus that the slags contain only very small percentages of P_2O_5. In addition, our enormous deposits of phosphate rock and large output of sulfuric acid have made it possible to obtain water-soluble phosphates at such a low price that it is difficult for basic slag to compete with them.

DEGREASED BONE

As previously pointed out, raw bone is an uneconomical and relatively ineffective phosphate fertilizer. The grease which it contains makes it diffi-

cult to grind and renders it so resistant to weathering influences and bacterial action that its decomposition in the soil is greatly delayed.

The removal of the fat or grease, however, changes the physical and chemical character of the bone rendering it friable, easily ground, and causing the P_2O_5 contained therein to be much more quickly available to crops. In addition, the oil or grease thus extracted constitutes a valuable by-product. While degreased bone is sometimes treated with sulfuric acid and its phosphate content rendered water-soluble, the usual practice is to apply it in a finely ground condition directly to the soil since experience has shown
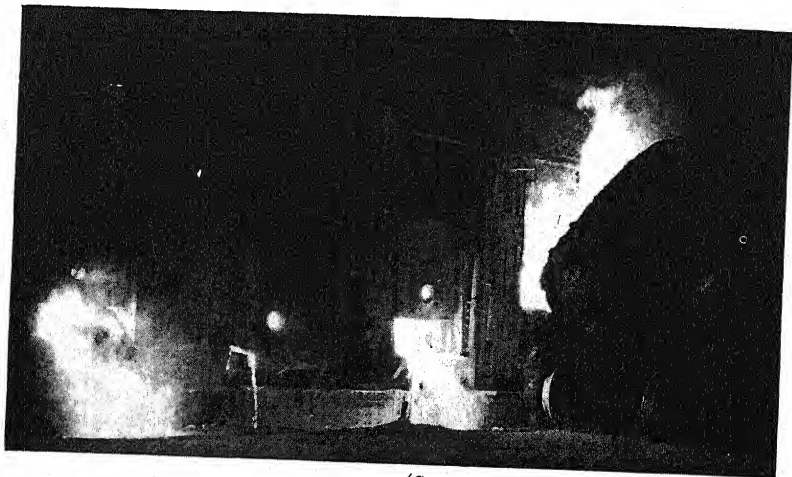
(Courtesy of Tennessee Coal, Iron and RR Company

FIGURE 2. The "Duplex" Process. At the right, high-phosphorus molten iron is being introduced into the open hearth furnace while basic phosphatic slag is being poured from the tap holes into receiving pots.

that it is an effective phosphate carrier even though less than one-half of its P_2O_5 content is soluble according to the conventional laboratory test for availability.

Degreased bone may or may not be subsequently treated to extract glue or gelatin. When used directly after being degreased the bone still contains a substantial percentage of organic nitrogen which adds to its value as a fertilizer or an animal feed supplement. If, however, the degreased bone is treated further to extract the glue the composition is again altered, the final product containing relatively little nitrogen, but being correspondingly richer in P_2O_5. Lambert[32] gives the following typical analyses of raw, boiled and steamed bone, as well as that extracted with benzine and subsequently degelatinized (Table 5).

The treatment of bones with organic solvents is the most effective way of extracting the grease and if the bones are to be subsequently used to recover glue or gelatin, this method is generally employed.

The raw bones are first sorted and passed over a magnetic separator to remove any tramp iron. They are then crushed, either between heavy-toothed rolls or in a hammer mill, and any bone dust screened out. To extract the grease from the crushed bone various organic solvents, such as benzine, carbon tetrachloride, gasoline and carbon disulfide have been tried, but petroleum benzine or naphtha is usually preferred. No solvent having a boiling point much above 100°C is suitable for this purpose.

Several types of extraction equipment have been proposed, but the following description of the plant and its operation is typical:

The equipment consists of one or more cylindrical tanks or extractors

TABLE 5. COMPOSITION OF RAW, DEGREASED AND DEGELATINIZED BONE

Ingredients	Raw Bone (%)	Boiled Bone (%)	Steamed Bone (%)	Fat Extracted and Degelatinized Bone (%)	
				(1)	(2)
Moisture	20.46	10.81	10.97	9.25	8.54
Organic matter	34.09	25.97	22.48	17.66	19.53
Tricalcic phosphate	39.21	53.15	57.17	62.39	61.22
Magnesia and lime carbonate	4.16	6.28	6.89	8.55	8.74
Alkali salts	1.14	0.27	trace	0.38	0.59
Silica	0.94	1.07	0.86	1.77	1.38
Contained nitrogen	3.63	2.45	1.74	0.97	1.05

fitted with filter plates or false bottoms and holding approximately ten tons of crushed bone. Each extractor is equipped with a charging door at the top for introduction of the stock and a similar door near the bottom for the removal of the fat-extracted product. These doors are closed and bolted when the plant is in operation. A pipeline (controlled by a valve) leads from an overhead solvent tank into each extractor (below the false bottom) and this space contains steam coils for heating the liquid solvent thus introduced. A valved outlet in the base of each extractor permits the grease and solvent emulsion to be drained into a still which is connected with a condenser for the recovery of the volatilized solvent. A pipeline (also controlled by a valve) leads from the top of the extractor to the same condenser. Separators are provided to separate water from the condensed solvent and permit the latter to be re-used.

In operating the plant, the crushed raw bone is charged into the extractor, and sufficient organic solvent introduced to cover the steam coils. The steam is then turned on, and extraction proceeds as the solvent vapor

is driven off, condensed by the column of stock and percolates back to the main body of liquid. After this first extraction, the valve controlling the outlet to the condenser is opened, and the solvent mixed with the water derived from the moisture in the bones is distilled off and condensed. The solvent is then separated from the water and re-used.

The operation is then repeated by introducing fresh solvent and after this second extraction the grease emulsion is drawn off and the solvent separated therefrom by distillation.

After the grease has all been removed, steam is blown through the column of extracted bone to drive off the last traces of solvent. The extractor is then opened and the bone allowed to dry.

The grease is then sent to the refinery and the extracted bone is either marketed directly as bone meal or treated further for the recovery of other products. A diagram of bone extraction equipment is shown in Figure 3.

Even if all the degreased bone produced were consumed for fertilizer purposes it would represent only a small proportion of the P_2O_5 entering into agriculture. But by no means is all of the degreased bone used in fertilizers, for bone is a very desirable and much sought raw material in the manufacture of bone black and its by-products (oil and ammonia). Moreover, a considerable tonnages of bones are also used in animal feed supplements and in the manufacture of glue and gelatin, yielding dicalcium or precipitated phosphate as a by-product. So important is bone black in the refining of sugar solutions and in the purification of certain vegetable oils, that its manufacture is described in a separate chapter (Chapter 27).

DICALCIUM PHOSPHATE

Although dicalcium phosphate is not a water-soluble compound it has much to recommend it as a soil amendment and were it not for the fact that it is more costly to produce than the water-soluble monocalcium phosphate, much greater quantities would be used for fertilizer purposes.

Theoretically, it would appear that dicalcium phosphate should be manufactured considerably more cheaply than monocalcium phosphate since it is intermediate between the latter compound and tricalcium phosphate. This is evident from consideration of the two following equations:

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow CaH_4(PO_4)_2 + 2CaSO_4$$

| *Tricalcic* | *Sulfuric* | *Monocalcic* | *Calcium* | (3) |
| *Phosphate* | *Acid* | *Phosphate* | *Sulfate* | |

$$Ca_3(PO_4)_2 + H_2SO_4 \rightarrow 2CaHPO_4 + CaSO_4$$

| *Tricalcic* | *Sulfuric* | *Dicalcic* | *Calcium* | (4) |
| *Phosphate* | *Acid* | *Phosphate* | *Sulfate* | |
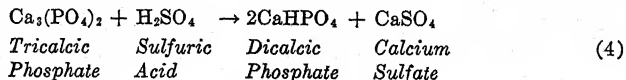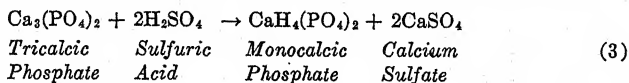
It is obvious that if reaction (4) took place, the amount of sulfuric acid

required would not only be one-half as great as that necessary for reaction (3), but the final product (a mixture of calcium sulfate and dicalcium phosphate) would be much more concentrated with respect to P_2O_5 and thus economies in transportation handling and distribution charges effected.
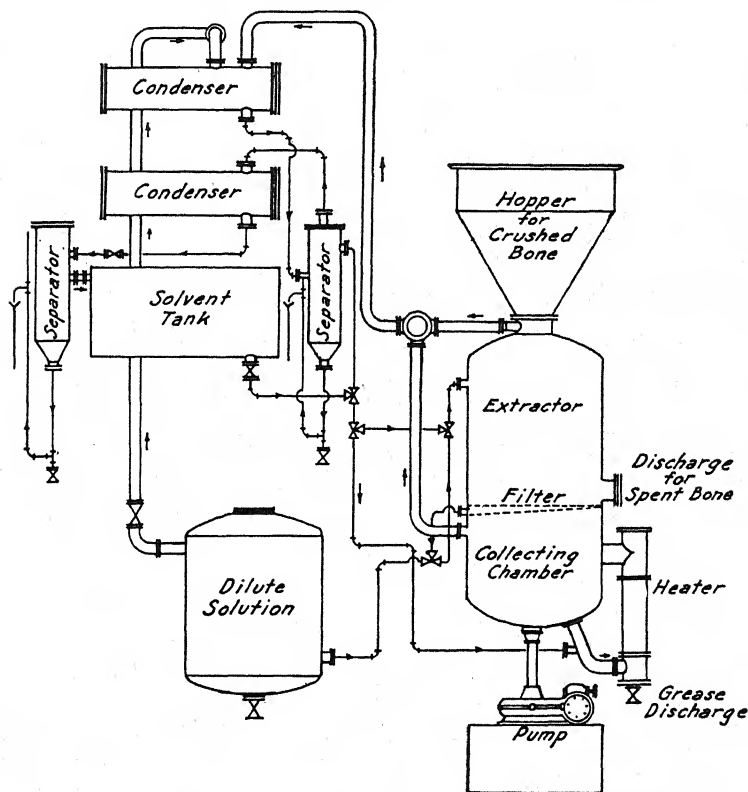
FIGURE 3. Type of equipment employed in de-greasing bone.

As pointed out in Chapter 15 efforts have been made to reduce the quantity of sulfuric acid normally employed in making superphosphate with a view to obtaining a product in which dicalcium phosphate is the predominating phosphate compound but only minor acid economies have been effected in commercial practice. Zbornik[40], however, claims to have converted the bulk of the P_2O_5 of phosphate rock into dicalcic phosphate of a citrate-soluble form by treating it with approximately one-half of the phosphoric acid normally required. This inventor mixed the acid and rock

in an autoclave maintained at temperatures between 130 and 220°C and at a pressure of more than 25 psi. Zbornik states that the moisture content of the mixture during digestion is a critical factor and should be maintained below 12 per cent. He employed phosphoric acid having a concentration of about 85 per cent H_3PO_4.

Ordinarily dicalcium phosphate is manufactured from phosphoric acid, or from water-soluble phosphates produced by the action of nitric or hydrochloric acid on bones or mineral phosphates. When either of these acids is employed in decomposing natural phosphates, the resulting solutions consist of mixtures of highly soluble salts which cannot be readily separated. Moreover, these solutions when evaporated to dryness or crystallized, yield salt mixtures having physical properties that render them unsuitable for fertilizer purposes.

Therefore, in order to obtain a usable phosphate product, the acid solutions are neutralized with lime or an alkali and dicalcium phosphate precipitated which can be filtered off, washed, dried and marketed as a fertilizer, for stock feed or as a mild abrasive.

After bones have been degreased either by a preliminary boiling or by extraction with benzine, they consist largely of tricalcium phosphate and an organic material known as ossein. On leaching degreased bone with weak hydrochloric acid (a 2 to 5 per cent solution) the tricalcium phosphate is completely dissolved, yielding a solution of monocalcium phosphate and calcium chloride:

$$Ca_3(PO_4)_2 + 4HCl \rightarrow 2CaCl_2 + CaH_4(PO_4)_2$$
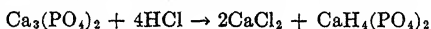
To this solution milk of lime is then carefully added in sufficient quantity to produce dicalcium phosphate:

$$CaH_4(PO_4)_2 + CaO \rightarrow 2CaHPO_4 + H_2O$$
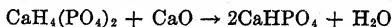
During the addition of the milk of lime filtered samples of the solution are tested from time to time to avoid an excess of base which would cause the formation of tricalcium phosphate.

The precipitate of dicalcium phosphate is then washed (with the minimum amount of water) free of calcium chloride in a filter press, dried and packed for shipment.

The undissolved residue resulting from the acid extraction of the degreased bone is soaked, limed, washed, neutralized and boiled to convert it into glue or gelatin, the manufacturing details of which are ably described by Bogue[27], J. Alexander[24], and Lambert[32], and therefore will not be treated here.

With a view to effecting an economy in the quantity of sulfuric acid required to decompose phosphate rock, Newberry and Barrett[34] proposed to treat this mineral with a mixture of sulfuric and hydrochloric acids

sufficient to form monocalcium phosphate, separate the calcium sulfate and insoluble residue from the acid solution by filtration, evaporate the latter to dryness and heat the dried product sufficiently high to drive off hydrochloric acid and convert the soluble salts into dicalcium phosphate. The hydrochloric acid is collected to be re-used. The reactions in their simplest form are as follows:

$$Ca_3(PO_4)_2 + H_2SO_4 + 2HCl = CaSO_4 + CaCl_2 + CaH_4(PO_4)_2 \qquad (5)$$

$$CaCl_2 + CaH_4(PO_4)_2 + heat = 2CaHPO_4 + 2HCl \qquad (6)$$
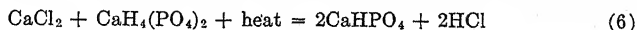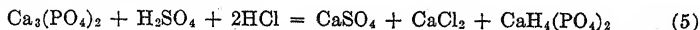
Theoretically, this process appears to have considerable merit since only one-half as much sulfuric acid is required as that employed in manufacturing water-soluble phosphate. In actual practice, however, the method has certain objectionable features: Unless the temperature at which hydrochloric acid is evolved is carefully controlled* highly insoluble calcium pyrophosphate is likely to be formed, yet unless the dried mass is sufficiently heated, a certain amount of calcium chloride will remain in the residue rendering it hygroscopic and unfit for fertilizer use.

Fox[29, 30] has patented a process somewhat similar to the above consisting in first producing monochlorophosphate ($CaClH_2PO_4 \cdot H_2O$), the manufacture of which is described in Chapter 18, then decomposing this compound with steam at a temperature of 200 to 400°C according to the following equation:

$$CaClH_2PO_4 \cdot H_2O + steam \rightarrow CaHPO_4 + HCl + H_2O$$
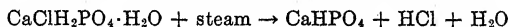
The inventor claims that under these conditions no calcium pyrophosphate is produced and the hydrochloric acid can be completely recovered and used to decompose further quantities of phosphate rock. As far as known, neither of these processes is being applied commercially.

Pike[35] has proposed to acidulate calcined phosphate rock suspended in water with hydrochloric acid till the P_2O_5 is completely converted into phosphoric acid. The acid solution is then treated with finely ground limestone to produce a solution of monocalcium phosphate and calcium chloride. An amount of milk of lime is then added sufficient only to precipitate the P_2O_5 as dicalcium phosphate which is separated from the solution by filtration. The only possible advantage that this process appears to have is some slight saving in the cost of the neutralizing agent since limestone instead of the more costly milk of lime is used to neutralize the first hydrogen of the phosphoric acid.

A continuous process for producing dicalcium phosphate is described by Seyfried[38] consisting in passing waste HCl gas through a column of unground phosphate rock over which water is sprayed. The resulting solu-

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* Dicalcium phosphate loses water of constitution at temperatures above 220°C.

tion of phosphoric acid, monocalcium phosphate and calcium chloride is continually withdrawn from the base of the tower as fresh rock is fed into the top. The acid solution is then partially neutralized with lime in a separate chamber to produce dicalcium phosphate.

Most processes involving the use of nitric acid yield products containing mixtures of dicalcium phosphate and other salts. Such products usually contain appreciable amounts of water-soluble P_2O_5 and are discussed in Chapter 18.

Curtis[28] proposes to produce dicalcium phosphate from phosphoric acid by means of limestone rather than milk of lime. The process consists in adding coarsely ground limestone to the acid until it is converted into a solution of monocalcium phosphate, then mixing this solution with a slurry of very finely ground limestone to effect the conversion of monocalcium into dicalcium phosphate. MacIntire[33] also has patented a somewhat similar process using highly concentrated phosphoric acid and finely ground limestone. It is obvious that neither of these processes is applicable to the economic manufacture of dicalcium phosphate for fertilizer purposes.

A number of processes have been patented covering the manufacture of dicalcium phosphate through the medium of sulfur dioxide and sulfurous acid[25, 26, 37, 39].

Bogue[27] describes the following three-step process for producing dicalcium phosphate from degreased bone: The first step consists in continuously circulating a saturated solution of sulfur dioxide over the crushed bone in a closed container, maintaining an acidity sufficiently high to keep the mineral matter in solution as monocalcium phosphate and calcium acid sulfite. In the second step the decanted solution is treated with steam, resulting in the precipitation of a mixture of dicalcium phosphate and normal calcium sulfite with the regeneration of part of the sulfur dioxide. In the third step, the balance of the sulfur dioxide is recovered by treating the mixed precipitate with sufficient hydrochloric acid to convert the calcium sulfite into calcium chloride leaving the dicalcium phosphate undissolved.

These three steps are represented by the equations given below:

$$\text{Leaching Step: } Ca_3(PO_4)_2 + 4SO_2 + 4H_2O \rightarrow CaH_4(PO_4)_2 + 2CaH_2(SO_3)_2 \quad (7)$$

$$\text{Steaming Step: } CaH_4(PO_4)_2 + CaH_2(SO_3)_2 = 2CaHPO_4 + CaSO_3 + SO_2 \quad (8)$$

$$\text{Regeneration of } SO_2: CaSO_3 + 2HCl = CaCl_2 + SO_2 + H_2O \quad (9)$$
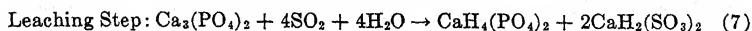
Whereas sulfur dioxide reacts with the calcium phosphate in bone, it is not effective in decomposing phosphate rock[31]. The effect of sulfur dioxide and sulfurous acid on the natural phosphates is discussed in Chapter 18.

The reactions whereby a mixture of phosphoric acid and calcium sulfate

is converted into dicalcium phosphate and ammonium sulfate by means of ammonia are described and discussed in the Chapter 17.

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20. Calcined, Fused and Defluorinated Phosphates

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INTRODUCTION

The various processes for rendering phosphate rock soluble in 2 per cent citric acid or a solution of neutral ammonium citrate by heating it to relatively high temperatures alone or mixed with silica, silicates and an alkali salt or with a magnesium mineral are covered in 'this chapter. Calcined superphosphate and triple superphosphate are also included since these products because of their low fluorine content offer possibilities as animal feeds.

Until the role that fluorine plays in phosphate rock was disclosed, most of the processes proposed and patented for producing available phosphates by calcination were based on false premises due to little or no knowledge of the factors which affect the solubility of natural phosphates. Earlier products were seldom uniform and the results could not be duplicated in commercial practice because of variations or irregularities in operating technique.

HISTORY OF EARLIER PROCESSES

Calcined apatite or phosphate rock is valuable both as a fertilizer and as a mineral supplement to animal feeds. As a fertilizer, it is not essential that fluorine be completely eliminated from the natural rock as long as the phosphorus component has the required degree of solubility. However, for use as a mineral supplement in livestock and poultry feeds, fluorine, being toxic, must be almost completely eliminated[61].

Pure mineral fluorapatite has a composition represented by the formula $Ca_{10}F_2(PO_4)_6$, the fluorine content of which is 3.77 per cent. Natural phosphate rocks, such as Florida land pebble and hard rock, are similar to

apatite, but might possibly contain within the apatite lattice once or more substituted elements or radicals[25, 29]. In addition to the substituted elements or radicals within the lattice itself, other constituents are present such as carbonate of lime, oxides of iron and aluminum, quartz, sulfur, magnesia, the alkali metals, and trace elements. An excess of fluorine over the theoretical amount required for the fluorapatite formula is usually present. Natural phosphate rocks vary in fluorine content from less than 1 to over 4 per cent[29].

With the idea of doing away with the use of sulfuric acid for the manufacture of soluble phosphates, investigators have spend considerably time and effort on calcination processes. In this process phosphate rock is heated with one or more cheap reagents intended to either bring about the decomposition of the mineral or so alter its physical structure that the product conforms to the conventional tests specified as measures of agricultural availability. While available phosphates produced by calcination processes would meet a demand in certain sections where an acid phosphate is not desired, these processes have been investigated chiefly for economic reasons since they seem to offer a means of utilizing low-grade phosphate rock or mineral phosphates containing certain impurities which render them unfit for treatment with sulfuric acid. Even where lower grades of phosphate are treated by calcination the final products usually contain higher percentages of P_2O_5 than ordinary superphosphate. Therefore if the cost of producing the unit of available P_2O_5 were no less than that obtained by the sulfuric acid method, the saving effected in transportation and handling charges on the more concentrated products should give the latter a considerable economic advantage[59].

Although much research work has been conducted on calcination processes, there is comparatively little recorded outside of the patent literature. Among the processes described below a few appear to have been commercially successful, but in most instances certain mechanical or chemical problems have arisen which made it difficult to obtain a product in which the P_2O_5 was uniformly available[59]. It is the writers' belief that the inconsistent results obtained on a commercial scale were due primarily to inconsistent fluorine removal. In most calcination processes the phosphorus availability increases as the fluorine decreases. This is particularly true in processes requiring a temperature of 2400°F (1316°C) and above.

Phosphate Rock, Silica and Lime

There are a number of patents in which it is claimed that heating phosphate rock with silica alone, or with silica and an alkaline earth compound, brings about reactions by which the phosphate is rendered citrate soluble. In the processes of DeChalmot[14] and Downs[16] mixtures of phosphate rock

and sand were heated with the idea of bringing about a combination between the silica and phosphate rock, producing a compound somewhat analogous to that found in slag obtained by the basic open-hearth or basic Bessemer process. The final product is said to contain an average of 20 to 22 per cent of P_2O_5, all of which is soluble in 2 per cent citric acid[59].

In the process of Stead[56] both lime and silica are mixed with phosphate rock and the mass heated to a smelting temperature. In order to reduce the melting point of the mixture, mill cinder or some iron bearing mineral is added. The inventor claimed that a product containing a compound of the definite formula $Ca_5P_2SiO_{12}$ is obtained, which is readily available under soil conditions[59]. Tromel[58] proposes adding CaO and SiO_2 to phosphate rock, and calcining at about 1450°C to produce a compound $9CaO \cdot P_2O_5 \cdot 3SiO_2$ or $16CaO \cdot P_2O_5 \cdot 5SiO_2$.

Phosphate Rock and Potash Silicates

With the idea of obtaining both potash and phosphoric acid in available forms, a number of investigators have proposed mixing a potash-bearing mineral such as feldspar with the phosphate charge and heating the mixture to a temperature where double decomposition occurs. Typical examples of such processes are those of Meriwether[40], Cowles[9] and Delacourt[15]. In none of these processes is a soluble alkali metal compound used. Cowles[10] proposes to heat a mixture of phosphate rock and a potash-bearing silicate in a rotary kiln to a temperature ranging between 1000 and 1700°C. The two minerals are mixed in such proportions that two molecular weights of lime are present for each molecular weight of silica. The inventor assumes that the phosphoric acid in the resultant product is combined with potash and alumina and that the lime is largely in the form of silicate.

Delacourt's process is similar to that just described, except that free silica is mixed with the charge in addition to that present in the potash silicate. This investigator further stipulates a temperature of 1000 to 1100°C and the maintenance of oxidizing conditions to prevent the reduction of P_2O_5. The product, it is claimed, consists of a mixture of potassium calcium phosphate and calcium silicate[59].

Phosphate Rock, Alkali Salts and Silica

In the process of Day[13] phosphate rock containing $CaCO_3$ is said to be made available by heating above calcination temperature, but below fusion. The reaction is greatly facilitated and the reaction time reduced by having a suitable proportion of silica present. Alkali salts such as kainite, KCl or K_2SO_4 may be added to reduce the temperature of reaction. Wolters[64] proposes fusing phosphate with alkaline earth and alkali silicates

above 1200°C. Heating with alkali silicates alone is harder to work and does not give as high citrate availability as that obtained with mixed silicates. Lowman[33] proposes making a fertilizer material by heating phosphate rock, sodium chloride, burned dolomite or magnesium limestone, and fluorspar. In the processes of Rothe[50] various combinations of phosphate rock, alkali oxide as salts (such as K_2SO_4), alkali chloride, silica, calcium or magnesium carbonate are heated in excess of 900°C with steam present.

Phosphate Rock and an Alkali Metal Hydroxide or Carbonate

Wiborgh[62], Conner[8], Newberry[44], Galt[21], and Stoppani and Volpato[57] have proposed heating to bright redness in a suitable furnace intimate mixtures of finely ground phosphate rock and an alkali metal hydroxide or carbonate until a sintered or semi-fused mass is obtained.

While the same general principle is followed in all of the processes listed above, the mode of procedure and the proportions of the several ingredients used are varied by the inventors. There also appears to be a wide difference of opinion regarding the chemical reactions involved[59].

Phosphate Rock and an Alkali Metal Salt

Probably the calcination processes which have received the most thorough investigation are those in which an alkali metal compound (usually Na_2SO_4 or $NaHSO_4$) is mixed with phosphate rock in relatively small quantities and heated in a furnace to a temperature where the acid radical of the salt is volatilized. Frequently part of the alkali base is volatized as well. This general scheme is varied by a number of inventors, silica, silicates or carbonates being used in addition to the alkali salt mentioned above. Typical examples of these processes are furnished by the patents of Newberry and Barrett[45], Newberry and Fishburne[46], Landis[32], Soper[55], Kreiss[31] and Meyers[41]. Practically all of these inventors agree that in order to obtain a product in which P_2O_5 is readily available it is necessary that the mass be thoroughly impregnated with the alkali metal compound during the early stages of heating, and that the mixture be maintained in a porous condition throughout the operation. The temperatures specified by the various inventors range all the way from 1000 to 1500°C[59].

In the process of Shoeld[51] a phosphate slurry containing 20 to 30 per cent Na_2SO_4 is heated suddenly (1 to 5 seconds) by injecting it into the central section of a rotary kiln so as to avoid the low temperature sintering zone.

Guernsey and Yee[23] made a rather extensive study to determine the optimum composition and conditions for calcining a mixture of phosphate rock, sodium sulfate and powdered coal. They found that best results were obtained when a charge consisting of 100 parts phosphate rock, 15 parts

sodium sulfate (as Na_2SO_4), and 15 parts of powdered coal was calcined at 1300°C for 25 to 30 minutes. The product obtained was 90 per cent citrate soluble.

PRESENT COMMERCIAL PROCESSES

Generally speaking, the method of producing available P_2O_5 from phosphate rock by calcination or fusion at elevated temperatures may be divided into two groups:

(1) Those based on chemical reactions between the rock and an alkali salt or magnesium silicate.

(2) Those based on the removal of fluorine through volatilization.

In group (1) the solubility of the phosphate is brought about primarily by the chemical reaction which takes place between the phosphate rock itself and the added reagents which are usually silica, silicates, an alkali salt or a magnesium mineral. In such processes complete removal of fluorine is not essential for high fertilizer availability, but normally 50 per cent or more of the fluorine is eliminated and a fused product is obtained.

At the present time there are at least two commercial processes for producing soluble phosphate without defluorination, namely, the Rhenania process and fusion of phosphate with magnesium silicate. Rhenania phosphate has been produced in Germany for a number of years, while calcium magnesium phosphate is a relatively new product that is now being produced by the Permanente Metals Corporation, Permanente, California, and by Manganese Products, Inc., Seattle, Washington.

In group (2) available phosphates are obtained primarily by eliminating fluorine from the phosphate rock, although certain reagents may be added to facilitate removal of fluorine, and these actually take part in the chemical reactions. This group of processes normally requires a temperature of at least 2400°F (1316°C) and usually the temperatures should be above 2600°F (1427°C). Defluorination may take place without fusion or by actually melting the phosphate rock. In most cases for effective defluorination water vapor must be present. Fluorine is normally volatilized as HF. Another normal essential for high solubility is quick cooling of the calcined product to prevent the P_2O_5 from reverting to an insoluble form. This is usually accomplished by quenching the hot product with air or water. In this type of process the fluorine in the final product should be below 0.20 per cent to obtain a high fertilizer availability.

Rhenania Phosphate

Of the various processes proposed for making available phosphates by thermal treatment of phosphate rock with alkali salts, few have been successful in attaining production on a commercial scale. In Germany,

however, there is a product known as Rhenania phosphate which has been manufactured for a number of years. Full information on the process and of the product is given in a report by Hawes and Lea[24], from which the following description is taken:

The Rhenania Phosphat Werke, a subsidiary of Kali-Chemie, at their plant at Brunsbuttelkoog, is producing a basic phosphate fertilizer by sintering a mixture of phosphate rock, soda ash, and sand in rotary kilns. Methods and operating technique have gradually improved, and the available phosphorus has been increased from 12 to around 30 per cent. A conversion of 90 to 95 per cent of the P_2O_5 to a citrate-soluble form is being effected. It is claimed that its fertilizer value is equal to that of superphosphate, and it sells at the same price per unit of P_2O_5[24, 43].

Rhenania phosphate is sold in three grades according to solubility in neutral ammonium citrate with guaranteed available P_2O_5 content of 23 to 25 per cent, 25 to 27 per cent, and 27 to 29 per cent. The maximum production for any one month was 10,000 tons, and the annual maximum output was 107,000 tons. The process requires the exercise of very close control throughout all operations and experienced burners to calcine the material within the narrow limits required[24].

Plant and Equipment. Storage capacity of the plant is 100,000 tons of phosphate rock, 6,000 tons of sand, 1,000 tons of soda ash, and 10,000 tons of finished product. A coal-fired 11 x 1.7 meter rotary drier is employed for drying separately both the phosphate and sand. Capacity is 10 to 12 tons per hour. Sand is ground separately in a 8 x 1.5 meter 2-compartment ball mill with a grinding capacity of 2 to 3 tons per hour. The dry phosphate and dry ground sand are mixed and ground in a $5\frac{1}{2}$ x 1.8 meter single-compartment tube mill with input of 10 to 12 tons per hour.

There are four kilns approximately 35 x 1.7 meters. Three of these kilns have enlarged clinkering zones, and one is a straight cylinder[43]. They are lined with low-alumina block and fired with powdered coal. Natural draught is employed and dust is collected with an electrostatic dust collector and recycled to the feed. Cooling of the clinker is effected by four brick-lined coolers 10 x 1.2 meters without lifters[24].

Raw Materials. Phosphate rock from various sources was used which included Curacao, Kola concentrates, Kola lump, and North African phosphate.

Sand is brought from sand pits on the Keil Canal by lighters and transferred to storage at the plant. It contains about 92 per cent silica. Soda ash in bags or bulk is hauled from the works by rail or barge and dumped into a storage bin.

The company also used "Schwartz Lauge," a waste product from the paper industry, containing about 57 per cent sodium carbonate and 36

per cent combustible matter. It is said to work just as well as soda ash and is less expensive.
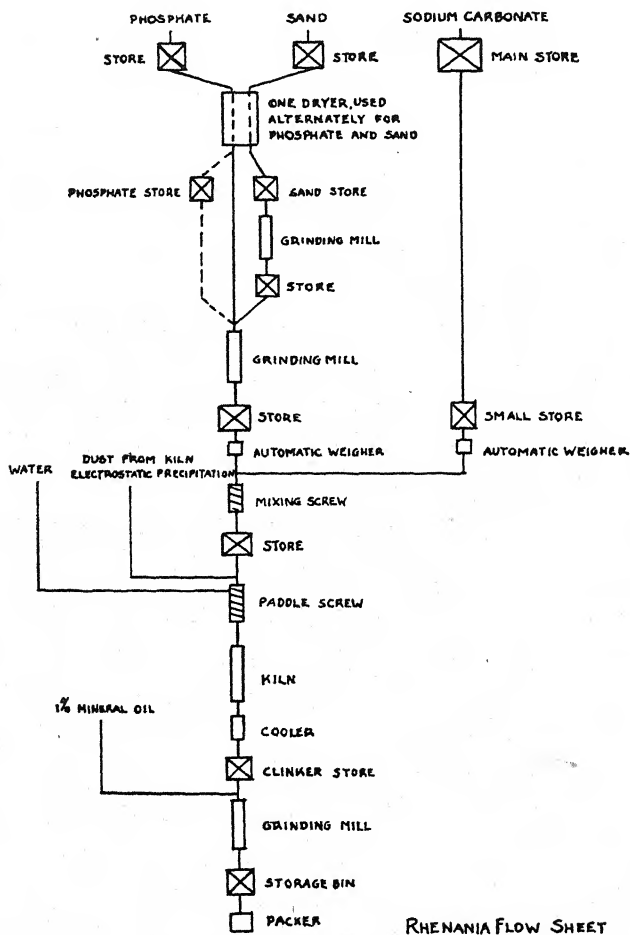
FIGURE 1. Rhenania Flow Sheet.*

Sodium sulfate has also been used as an admixture with soda ash in some of the operations, but it is said to require a higher mole ratio of the soda compounds to P_2O_5 than sodium carbonate, cause greater wear on

* J. R. Hawes and F. M. Lea, Phosphates Kali-Chemie, Brunsbuttelkoog. (P. B. Report 18913)

the kiln lining and involve the problem of sulfur compounds in the stack gases[43].

Bituminous slack coal used in this process should not contain over 6 per cent ash and about 25 per cent of volatile matter[43].

Chemistry of the Process. According to Hawes and Lea[24] the chemical reaction for pure fluorapatite can be expressed as follows:

$$2(9CaO \cdot 3P_2O_5 \cdot CaF_2) + 6Na_2CO_3 + 5SiO_2 \rightarrow 6(Na_2O \cdot 2CaO \cdot P_2O_5) + 4(2CaO \cdot SiO_2)$$
$$+ SiF_4 + 6CO_2$$
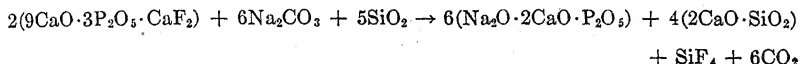
The SiF_4 is decomposed into SiO_2 and HF, and part of the latter is volatilized.

The compound in the product expressed by the formula $CaNaPO_4$ is soluble in neutral ammonium citrate[24].

Raw materials are proportioned to give a ratio of 1 mole of Na_2CO_3 to 1 mole of P_2O_5. Phosphate rock with a high fluorine content requires 1.1 to 1.2 moles of Na_2CO_3 per mole of P_2O_5[43]. The theoretical amount of silica required in the process is the amount necessary to combine with the CaO liberated by reaction to form $2CaO \cdot SiO_2$. Actually around 10 per cent in the raw mix is required, taking into account the SiO_2 present in the phosphate. Too much silica in the mixture tends to soften the load in the burning zone and gives trouble by excessive balling and the formation of sausages[24].

A typical mixture of raw materials with the use of Constantine phosphate contained 17 per cent Na_2CO_3 and 10 to 11 per cent of SiO_2. This produced a clinker containing about 26 per cent total P_2O_5 and 24 to 25 per cent P_2O_5 soluble in ammonium citrate[24].

Operation of the Process. Dry sand previously ground to a fineness of 85 to 95 per cent passing a sieve having 4900 openings per square centimeter (about 170 mesh) is proportioned and mixed with dry phosphate rock and fed to a tube mill. The mixture is ground to a fineness of 50 per cent minus a 4900 screen. A typical mixture is 1,000 parts of phosphate rock and 115 parts of sand (92 per cent SiO_2). The phosphate-sand mixture is proportioned and mixed with soda ash by synchronized automatic weighers and mixing screws. It is then elevated to one of five storage hoppers having a total capacity of 600 tons. From here the material is conveyed to a paddle screw where it is dampened with 10 per cent water and fed to the kilns. The dust recovered by the electrostatic precipitator is added at this point. The amount of dust varies between 4 and 10 per cent[24].

The kilns are fired with coal which is dried and ground in a ring roll mill. The speed of the kilns is 1 revolution in 55 and 1 revolution in 80 seconds. The capacity of each kiln is 4 to 5 tons of clinker per hour "with a coal consumption of about 15 per cent." The slope is 1 in 25. Tempera-

tures in the hot zone are 1100 to 1250°C. The temperature of exit gases from the kilns is about 400°C. The maintenance of temperature is very critical. "Incipient fusion" is allowed to the extent of a certain amount of "climb" on the kiln walls. "Distinct fusion" is prevented by reducing the fires[24].

Water is introduced into the burning zone by a jet at the rate of approximately $\frac{1}{2}$ gallon per minute. Water vapor is considered essential for driving off the fluorine in sufficient amounts to obtain the maximum citrate solubility[24]. The clinker, however, contains from 1.25 to 2.50 per cent fluorine, which in itself does not show sufficient fluorine removal to obtain the solubility effected by the defluorinating processes used in the United States.

TABLE 1. ANALYSES OF RHENANIA PHOSPHATE

	Kola Concentrate Clinker (%)	Curacao-Constantine Clinker (%)
Ignition loss	0.60	
SiO_2	10.54	9.84
Fe_2O_3	0.71	0.34
Al_2O_3	1.53	0.56
CaO	40.05	43.10
Na_2O	15.43	13.41
K_2O	0.30	0.23
P_2O_5	29.09	31.19
F	2.19	1.26
SO_3	0.20	
P_2O_5 soluble in citric acid	28.00	28.00

Mud rings are formed in the feed end of the kilns; clinker rings are formed in front of and in the rear of the burning zone, which build up and seriously affect combustion. The mud rings and the clinker rings behind the burning zone are usually removed by shifting the flame. Those close to the discharge end are eliminated by poking with an iron bar. When any of these rings become so large that they cannot be eliminated otherwise, it is necessary to shut down the kiln and remove them by hand[43].

The material as it comes from the kiln is slightly sticky and builds up in the chute leading to the cooler. A small stream of water sprayed in the chute eliminates this difficulty[43]. The product is discharged from the kiln at about 1150°C and its temperature is reduced to 400 to 600°C in the cooler. It is then crushed to about 25 centimeters in size, conveyed to the clinker storage bins, and later ground to a fineness of 85 per cent or more through a 4900 screen in ring-type grinding mills and stored in an open warehouse. One per cent of mineral oil is added to the grind to prevent dusting[43].

Finished Product. The finished product is packed in open-mouth paper bags for shipment by a Mackeson of Hanover packer. The capacity of these machines, which come in two sizes, are 8 and 16 tons per hour respectively[24]. Hawes and Lea[24] give the analyses of Rhenania phosphate in Table 1.

The analyses of a sample taken from this plant in 1949 by the writers are given in Table 2.

The producers of Rhenania phosphate claim that it is insoluble in water but available to plant life, that it does not revert and can be successfully mixed with nitrogenous and potassium-containing fertilizers[43]. However, in view of its basic character the writers of the report doubt the wisdom of mixing it with large proportions of ammonium salts.

TABLE 2

	Ground Product (%)
P_2O_5 Total	24.70
P_2O_5 Available 2% citric acid	23.62
P_2O_5 Available neutral ammonium citrate	23.35
SiO_2	12.43
Fe_2O_3	0.59
Al_2O_3	1.37
CaO	42.08
F	2.40
Na_2O	12.65

Röchling Phosphate

Maclennan *et al.*[37] describe a product somewhat similar to Rhenania phosphate which has been produced on a pilot-plant scale by Röchling'sche und Stahlwerke and others at Völklingen, Saar, Germany. Instead of using soda ash and sand, soda slag (a waste material from the desulfurization of iron with sodium carbonate) is fused with phosphate rock to make a basic phosphatic fertilizer. A conversion of better than 90 per cent of the phosphate constituent to the citrate soluble form is claimed for the process.

The following advantages were claimed for this process over that for Rhenania phosphate. Instead of using three raw materials (phosphate rock, sand and soda ash) which require very careful proportioning and properly controlled kiln conditions the Röchling process requires only two materials (phosphate rock and soda slag). The latter contains the necessary ingredients for the decomposition of fluorapatite, namely, Na_2O and SiO_2. The kiln feed does not have to be ground, and proportioning of the raw materials and control of burning conditions are not critical[37].

Experimental work was carried out in two small rotary kilns and a new type of refractory lining was developed for the burning zone consisting of a

mixture of tar and ground dolomite, and was made either in the form of "concrete" or brick. A longer life over other refractories was claimed for this material[37].

Soda slag was obtained from Völklingen, Saar. Following is a breakdown of its composition, according to Maclennan[37]:

	(%)
Na_2O	23–35
SiO_2	22–34
Fe	3–10
Mn	2–8
CaO	3–10
MgO	1–5
Al_2O_3	2–5
S	5–12
P_2O_5	0.2–3
V	0.1–0.9

Slags in which CaF_2 was used as a flux are not desirable due to the formation of insoluble fluorapatite. Any type of phosphate rock is said to be suitable for the process, with a preference for a high content of R_2O_3 to assist in fusion. A material 5 to 10 mm, such as Florida pebble, was found most desirable. The process is carried out as follows:

Soda slag is crushed to 5 to 10 mm in size and metallic iron is removed by magnetic separation. Soda slags of different analyses are mixed to obtain correct proportions and small amounts of Na_2CO_3 and $CaCO_3$ are added if necessary. Phosphate is used as received. Raw materials are proportioned by weight to obtain a molar ration of 1 to 1.2 Na_2O to 1 P_2O_5, mixed in a mixing screw conveyor, and fed to the kiln. Powdered coal is used for fuel. Fusion of the charge and completion of the reaction is accomplished at 1100°C. Flue dust is re-cycled to the feed. An average of 25 tons per day was produced in the pilot kiln. Each ton of clinker requires 0.5 to 0.6 tons of phosphate and 0.50 to 0.58 tons of soda slag. The molten slag is discharged from the kiln at a temperature of 1000°C into a cooler where its temperature is reduced to about 300°C. Contrary to the usual practice in nearly all calcining processes where quick cooling is required to retain or increase availability, it was found in this process that quick cooling reduced the availibility of the phosphate constituent from 2 to 5 per cent[37].

The cooled clinker is ground in ball mills to a fineness of about 90 per cent through an A.K. 16 sieve and packed in bags for shipment.

The main reaction involved can be expressed by the following equation:

$$2(9CaO \cdot 3P_2O_5 \cdot CaF_2) + 6Na_2O + 5SiO_2 \rightarrow 6(Na_2O \cdot 2CaO \cdot P_2O_5)$$

$$+ 4(2CaO \cdot SiO_2) + SiF_4\text{[37]}$$
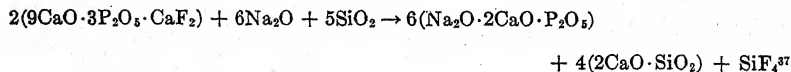
Analysis of a typical sample taken from a run in which Florida pebble was used is as follows:

	(%)
P_2O_5 Total	19.81
P_2O_5 Ammonium citrate soluble	18.60
CaO	32.00
SiO_2	19.80
Na_2O	12.90
MgO	3.60
Al_2O_3	4.10
Fe	3.60
S	0.20
F	0.30

According to information furnished in 1946 by Maclennan *et al.*[37], "experimental work had been completed, the pilot plant had been dismantled, and a full scale plant at Mannheim/Rheinau was nearly ready for operation by a new company called Hutten Chemie G.M.b.H." The plans were for an annual capacity of 60,000 tons. As their "intended source of supply of soda slag lies in the French zone of Germany," it is not known if they are experiencing difficulties in obtaining this raw material. In conclusion Maclennan[37] states that "the process appears to be technically sound," but "results" should be confirmed by "full scale production over a period of time." "Economic production would depend on a cheap supply of suitable soda slag."

Calcium Magnesium Phosphate

This new type of phosphate fertilizer has been referred to as phosphate rock magnesium silicate glass[28]. An article was published in 1943 by Walthall and Bridger[60] describing the preparation of an available phosphate fertilizer by fusion of phosphate rock and olivine. The P_2O_5 and MgO constituents were both rendered available to plants. Since these experiments were run considerable interest has been taken in this type of product. The process has been developed from the laboratory through the pilot-plant stage to large-scale production[42]. It is now being produced by the use of both serpentine and olivine.

Fused calcium magnesium phosphate, a product made by the Permanente Metals Corporation at Permanente, California, is on the market under the name Thermo-Phos[6, 7].

Raw materials consist of western phosphate rock and serpentine (a hydrated magnesium silicate) which is obtained from a local deposit. The raw materials are proportioned and fed to two converted electric furnaces where the charge is fused. The molten material after being tapped from

the furnaces is granulated, dried, ground and bagged for shipment. The output of the plant is given at 6,000 tons monthly[6, 7].

Thermo-Phos contains around 18 per cent P_2O: and 15 to 17 per cent MgO. Therefore, this fertilizer is a source of magnesia as well as phosphorus. It is claimed to have been used successfully on various types of soils. While it can be applied directly to the soil, the major portion of the output is used in mixed fertilizers[7].

Manganese Products, Inc., Seattle, Washington, is producing calcium-magnesium phosphate fertilizer by fusing in an electric furnace a proportioned mixture of phosphate rock and olivine (a magnesium iron silicate). The conditions in the Northwest are favorable for the operation of the process, with an ample supply of raw material and a ready market for the product[42].

Moulton[42] in a recent article describes the process as follows:

Phosphate rock is mined at the Company's mine at Flint Creek Valley, near Phillipsburg, Montana, and hauled by rail to the plant at Seattle. It contains 30 to 32 per cent P_2O_5. Olivine is brought by barge from Cypress Island, near Anacortes, Washington. The ore contains around 8 per cent iron, as Fe_2O_3. Both of the raw materials are crushed to -1.5 inch in size before shipment to the plant. In the rainy season they are dried in a rotary drier to a moisture content of around 1 per cent. The phosphate rock and olivine are proportioned approximately two parts of phosphate to one part of olivine, and fed to a conveyor belt which discharges into the furnace hopper.

The furnace is a converted three-phase Green electric arc steel type now 10 feet high and 5 feet, 8 inches in diameter inside of the refractory lining. It is equipped with three 6-inch graphite electrodes, which are consumed at the rate of 15 pounds per ton of rock[20, 22, 42]. The electric power requirements with the present capacity are 5,000 amperes and 180 volts and power consumption is at the rate of 850 kw-hours per ton of product. The furnace lining consists of carbon paste rammed in the bottom of the furnace. The part of the shell that comes in contact with the molten material is not lined, but is cooled by a water jacket which forms a solidified coating of slag on the inside of the shell. The portion of the shell above the melting zone is lined with fire brick[42].

The furnace is charged continuously, and operates at about half the capacity of 10 tons within the crucible. The fusion time is one to two hours and the operating temperature about 1500 to 1600°C. A ton of mixed feed yields 0.9 to 0.95 tons of fused product[20, 42]. A large portion of the iron constituent in the olivine is reduced to the metallic state and is tapped at the lower hole of the furnace. The gases from the furnace consist of water vapor, H_2, N_2, CO, CO_2, and fluorine compounds[42].

Tapping is done for 30 minutes with 5-minute intervals between. The molten slag flowing out is quenched with jets of water under high pressure to prevent the phosphate from reverting to an insoluble form. The quenched material is broken into granules of about 20 mesh in size, and is moved
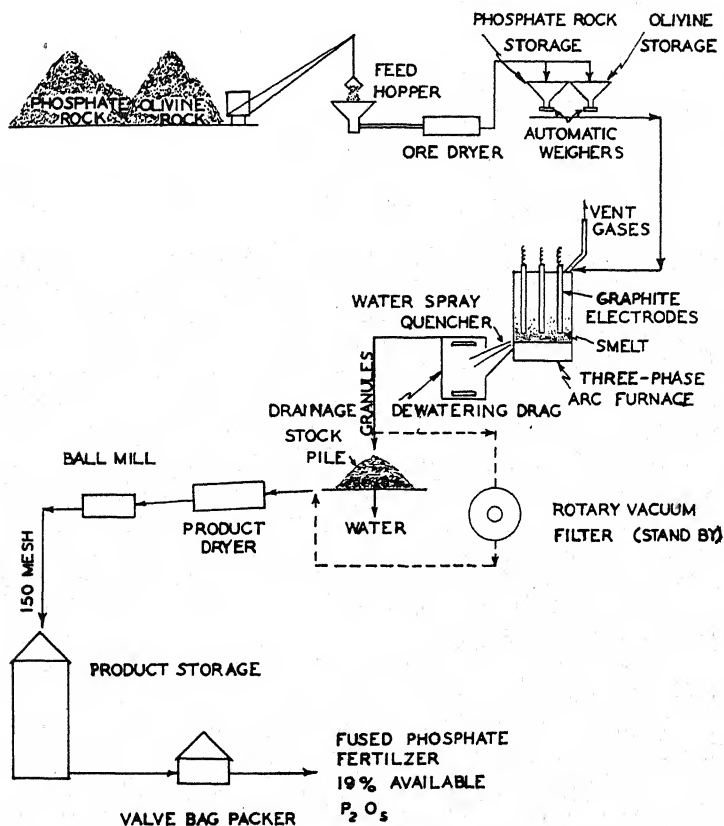
FIGURE 2. Flow sheet of calcium magnesium phosphate plant.*

from the bottom of the quenching tank by an inclined scraper flight conveyor and then conveyed to a stock pile, where it is allowed to drain. The product is dried to less than 1 per cent moisture in an oil-fired rotary drier, ground to 150 mesh in a ball mill, and packed in 100-pound bags for shipment. The present capacity of the plant is 50 tons per 24 hours, but it is reported that plans are under way to greatly increase the output[20, 22, 42].

* R. W. Moulton, Manganese Products, Inc., *Chem. Eng.*, **56**, 102–04 (July, 1949).

The product is granular, free-flowing, does not cake, is non-acid, and non-hygroscopic. It contains at least 19 per cent available P_2O_5 and about 14 per cent MgO.

A typical analysis of this fused phosphate fertilizer is given by Moulton[42] as follows:

	(%)
P_2O_5 Total	22.5
P_2O_5 Available	19.0
CaO	29.0
MgO	14.0
SiO_2	23.0
F	1.8
R_2O_3	7–8

The nutrient value of the phosphate rock magnesium silicate glasses produced with the use of both serpentine and olivine have been studied by the U. S. Department of Agriculture[28]. When finely ground the growth response to these glasses was greater than that to triple superphosphate on certain soils. It was found that fineness was highly important to produce solubility and crop response.

Defluorination of Phosphate Rock

The calcination and removal of fluorine from phosphate rock on a laboratory scale has been studied by numerous investigators. Caldwell[5] describes a method of treating ground phosphate rock and carbonaceous material in an oxidizing atmosphere at 1400 to 1450°C to remove the fluorine. Jacob and his co-workers of the U. S. Department of Agriculture volatilized fluorine by thermal treatment in the presence of silica and water vapor. They have shown that treatment of small charges of phosphate rock in thin layers at 1400°C in an electric furnace with water vapor present removed 95 per cent or more of the fluorine. Better than 90 per cent of the phosphorus pentoxide content was rendered soluble in neutral ammonium citrate. The product was caked or sintered, but not fused[30, 47, 48, 49].

Bally[2] proposes making soluble phosphates by defluorinating free-falling phosphate particles in a vertical furnace, burning powdered coal. Fluorine is recovered in a scrubbing tower.

In the process of Curtis[11] phosphate rock is defluorinated and made citrate-soluble by heating at 1300 to 1400°C in water vapor atmosphere produced by the ignition of hydrogen in oxygen. Some silica is required for defluorination. Luscher[34] proposes calcining phosphate rock by recirculating steam after removal of fluorine gases. A tunnel type furnace with resistance heater is used. Luscher[35] also proposes to melt phosphate rock and silica and pass steam through the melt in a restricted zone.

Curtis[12] and others in small-scale tests defluorinated phosphate rock by fusion at temperatures 50 to 170°C above the melting point with water vapor present. Results were checked in semi-works oil-fired furnaces. Elmore[19] describes a method of removing fluorine from phosphate rock and rendering it available as plant food by mixing with acidic oxide material and heating to fusion temperature in the presence of water vapor.

An invention by Maust and Hollingsworth[38] describes the use of phosphate rock with less than 3 or 4 per cent silica, mixing about 5 per cent of aluminum phosphate with the rock, pelletizing and firing at 2700°F (1482°C) to 3000°F (1649°C) with plenty of steam in the kiln atmosphere. In addition, the nodules may contain 10 to 50 per cent of carbonaceous material which burns out at 1800 to 2400°F (982 to 1316°C), leaving porous nodules more open to the action of water vapor.

The chemical reaction that takes place when fluorine is volatilized from fluorapatite can be represented by the following equation:

$$Ca_{10}F_2(PO_4)_6 + H_2O + SiO_2 \rightarrow 3Ca_3(PO_4)_2 + CaSiO_3 + 2HF^{26}$$
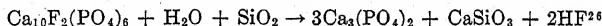
At the present time there are at least three processes employed for production of defluorinated phosphate. These processes are:

(1) Breaking the bond that holds the fluorine in the fluorapatite lattice by first treating the rock with some chemical such as sulfuric acid followed by thermal treatment.

(2) Fusion of phosphate rock in the presence of silica and water vapor.

(3) Thermal treatment (without fusion) of phosphate rock in the presence of silica and water vapor[61].

DEFLUORINATED SUPERPHOSPHATE

Several patents have been issued for defluorinating superphosphate. They are all based on calcining in calciners or rotary kilns. Wight and Anderson[63] describe a process for treating den or granular superphosphate in a rotary kiln at temperatures between 600 and 800°C to remove the fluorine and increase the availability of calcium and phosphorus for an animal feed supplement. Shoeld[52] proposes to reacidulate calcined superphosphate (in which the fluorine content has been reduced to around 0.1 per cent) with concentrated sulfuric acid and to heat the mixture to incipient SO_3 fumes thereby reducing the fluorine content to about 0.015 per cent. The object of the invention is to produce a solid, non-toxic, acidic phosphatic material.

Shoeld[53, 54] claims an improvement on the Wight patent by calcining superphosphate at temperatures above 800 to substantially 1200°C. The additional heat removes most of the sulfur combined as calcium sulfate

and converts practically all of the monocalcium phosphate to the tri-calcium form. The fluorine is subttantially all removed.

An invention by Butt[3] relates to processes of removing fluorine from superphosphate, triple superphosphate or a mixture of the two. To prevent fusion of triple superphosphate, which occurs at 300°C and higher, and to prevent evolution of sulfur gases from gypsum, which is present in super-phosphate, he proposes to add to the superphosphate a basic alkaline earth compound such as calcium carbonate, calcium oxide, hydrated lime or dolomite in amounts more than enough to neutralize the free acid present. The fluorine is then removed by calcining at a temperature of about 875 to 900°C. The product is soluble in 0.4 per cent HCl solution and the fluorine content reduced generally to a figure below 0.1 per cent. No analyses are given showing SO_3 content.

The production of defluorinated superphosphate on a commercial scale was started during the early part of World War II when there was a shortage of bone meal. Removing fluorine from superphosphate appeared to be a quick answer to the bone meal problem. At one time during this period there were at least four plants in operation[61].

The methods employed by all operators were similar, with certain varia-tions in calcining temperatures, time of detention, and material handling, etc. A general description of the process is given as follows:

Superphosphate, den or granular, is conveyed from storage to a feed hopper from which it is fed by a belt, screw, or other suitable type of feeder to a brick-lined rotary kiln. An iron bar, fastened by a swivel and chain, prevents the formation of mud rings in the feed end. The load is treated at temperatures varying from 800 to 1200°C, according to the required degree of conversion of the phosphate constituent. Jets of water are in-troduced into the hot material just before being discharged from the kiln to supply an excess of water vapor, which aids in defluorination. The prod-uct is in the form of nodules from $\frac{1}{8}$ to $\frac{1}{2}$ inch in size. The discharge from the kiln is conveyed to a cooler and then elevated to a hammermill which reduces it to about 60-mesh in size. After this it is put into a storage bin, and from here the product is bagged and loaded into cars for shipment. The fluorine is substantially all volatilized and the conversion of mono-and dicalcium to alpha and beta tricalcium phosphate depends upon the calcining temperature, detention time and amount of sulfur trioxide re-moved. The following analysis gives the P_2O_5 and fluorine content of a typical superphosphate before and after treatment:

Ingredient	Before	After
P_2O_4	20.79%	30.75%
F	1.54%	0.06%

Defluorinated Tricalcium Phosphate. Under the heading of defluorinated superphosphate there should be included a patent issued in 1948 in which Butt[4] describes a method for the manufacture of defluorinated tricalcium phosphate for an animal feed ingredient. Ground phosphate rock is mixed with material containing available P_2O_5 in amounts sufficient to bring the mole ratio between 2.7 and 3.1 in the final product according to the following formula:

$$\frac{\text{Moles of } CaO + MgO + Na_2O + K_2O - SO_3 - F_2}{\text{Moles of } P_2O_5 - Fe_2O_3 - Al_2O_3}$$

Phosphate rock ground to a fineness of about 94 per cent passing a 60-mesh screen is treated with 53.5°Bé phosphoric acid, in a suitable mixer, and dumped on a pile to cure from 1 to 24 hours. The mass is then reground to pass a 6-mesh screen and fed to a 6 x 80 foot cement-type rotary kiln having a pitch of about 1 inch in 8 feet, and revolving at the rate of about 2.5 rpm. The kiln is lined with refractory brick and is ribbed or corrugated on the inside to effect a tumbling action of the charge through the hot gases. Fuel oil is used for fuel. Feed to the kiln is at the rate of about 1,500 pounds per hour, and kiln discharge is at the rate of 1,100 to 1,200 pounds per hour. The calcining loss is about 20 to 25 per cent. The detention time of the charge in the kiln is about $1\frac{1}{2}$ hours[4]. Water vapor is introduced under certain conditions by a spray of water in the hot end. The temperature at the hottest point, which is about 8 feet from the burner, is around 1200°C. No mention is made of the formation of any coating on the inside of the kiln lining. An example is given of a mix of raw materials consisting of 100 pounds of phosphate rock containing 34.75 per cent P_2O_5, 49.35 per cent CaO, 3.85 per cent F, and 380 pounds of phosphoric acid containing 33.0 per cent P_2O_5, 1.4 per cent CaO, 1.9 per cent F, which by calcining yielded 1,050 pounds of product analyzing 45.5 per cent total P_2O_5, 45.5 per cent CaO and 0.038 per cent F[4].

It is claimed that triple superphosphate can be used instead of phosphoric acid in the process, provided that the desired mole ratio is maintained in the final product.

This process can be carried out successfully in two steps. In this case sufficient additional phosphoric acid or equivalent material is added to the mix to give to an intermediate product a mole ratio below about 2.7. The mixture is calcined at 1100 to 1200°C. The intermediate product is ground to about 50-mesh and mixed with a basic material such as lime to bring the mole ratio in the final product to about 3.0. It is then recalcined at around 1000°C.

It has been shown that the 2-step process is easier to practice than the 1-step process, and that the cost of production is probably no higher. At

least 80 to 90 per cent of the total P_2O_5 in the product is claimed to be in the form of tricalcium (*ortho*) phosphate, and the ratio of fluorine to P_2O_5 not more than about 1 to 300[4].

Fused Tricalcium Phosphate

In account of the difficulties experienced in the control of temperatures below the fusion point, the Tennessee Valley Authority concentrated their efforts on the removal of fluorine from phosphate rock in the molten state. Factors affecting the volatilization of fluorine from the fused rock were studied on a laboratory scale. According to Hignett and Hubbuch[26], it was found that the rate of defluorination was affected by the viscosity of the melt, the velocity of the furnace gases, the presence of water vapor, the depth of the molten charge, temperature, and chemical composition of the melt[18]. It was claimed that "under favorable conditions 90 per cent or more of the fluorine could be volatilized in 10 minutes." The phosphate constituent was found to be tricalcium phosphate[36], and the name fused tricalcium phosphate was given to the product[26].

Investigations were carried from the laboratory to the pilot-plant stage using several types of furnaces. The final type for demonstrating the use of the process was a cylindrical refractory-lined shaft, which was fired first by gas and later by fuel oil[26].

Results of field tests showed that fused tricalcium phosphate produced in pilot furnace operations was comparable on certain soils to concentrated superphosphate. Estimates based on operations indicated that the material could be produced at a low cost[26]. A demonstration plant was, therefore, constructed near Columbia, Tennessee, at TVA's phosphate mining and concentration plant. Operations were begun in June, 1945, and continued intermittently for a number of years. Improved semi-commercial units are now in production.

The furnace charge is a briquetted mixture of phosphate matrix and phosphate sand proportioned to give a 20 to 25 per cent silica content to the product. As described by Hignett and Hubbuch[26] the charge material, in the form of briquettes, is conveyed from the briquette storage bin to a hopper over the skip pit (Figure 4). It is dumped from there into a weigh hopper where it is weighed and dumped into the skip car, which elevates the charge to a charging hopper on top of the furnace. The capacity of a skip car is about 1 ton. It is discharged from the charging hopper into the furnace by opening a bell at the bottom of the hopper. The load to the furnace is controlled by the operator who makes frequent inspections at the access door. There are two cylindrical shaft furnaces approximately

43 feet high and 8 feet in diameter (inside of the refractory lining), Figure 4.

The furnace was originally equipped with 4 burner ports located at the bottom of the furnace, which were later changed to two and redesigned to improve efficiency. They are 30 x 10 inches and connected with the hearth of the furnace at a 30° downward angle. The 2 burners are fired with grade 5L fuel oil at about 225°F (107°C). Air for combustion is furnished by air compressors at 3 to 10 psi at the burners. The charge is melted and settles to the hearth of the furnace. It is tapped at approximately one-hour intervals and the molten phosphate is discharged into a brick-lined trough
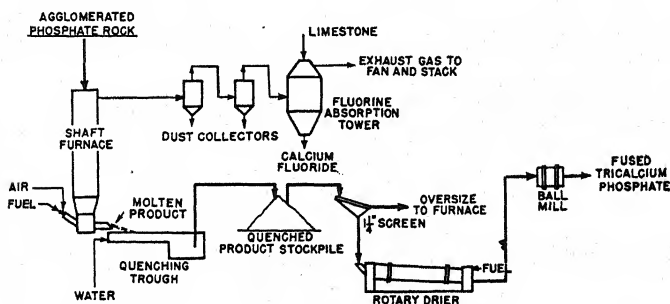
(*Courtesy of TVA*)

FIGURE 3. Flow diagram of process for defluorination of phosphate rock by fusion.

where it is quenched with jets of water of high velocity. When tapped from the furnace the temperature of the melt is around 2550 to 2700°F (1399 to 1482°C). The water and granulated material empties from the trough into a pit from which the water overflows and is re-cycled. The wet product is picked up with a bucket crane and dumped on storage. It is then screened through a 1¼-inch screen. The oversize is returned to the furnace and the undersize is dried in an oil-fired rotary drier. The dried material is screened and the oversize is reduced in a hammermill to pass a 10-mesh screen. It is then packed in bags and loaded in cars for shipment. The gases from the furnace go to the fluorine recovery process (see flow sheet, Figure 3).

Data pertaining to the operation of the Columbia plant are given by Hignett and Hubbuch[26] as follows:

The output of the 2 furnaces is around 150 tons in 24 hours. A feed of 1.12 tons is required to produce 1 ton of product. About 50 gallons of fuel
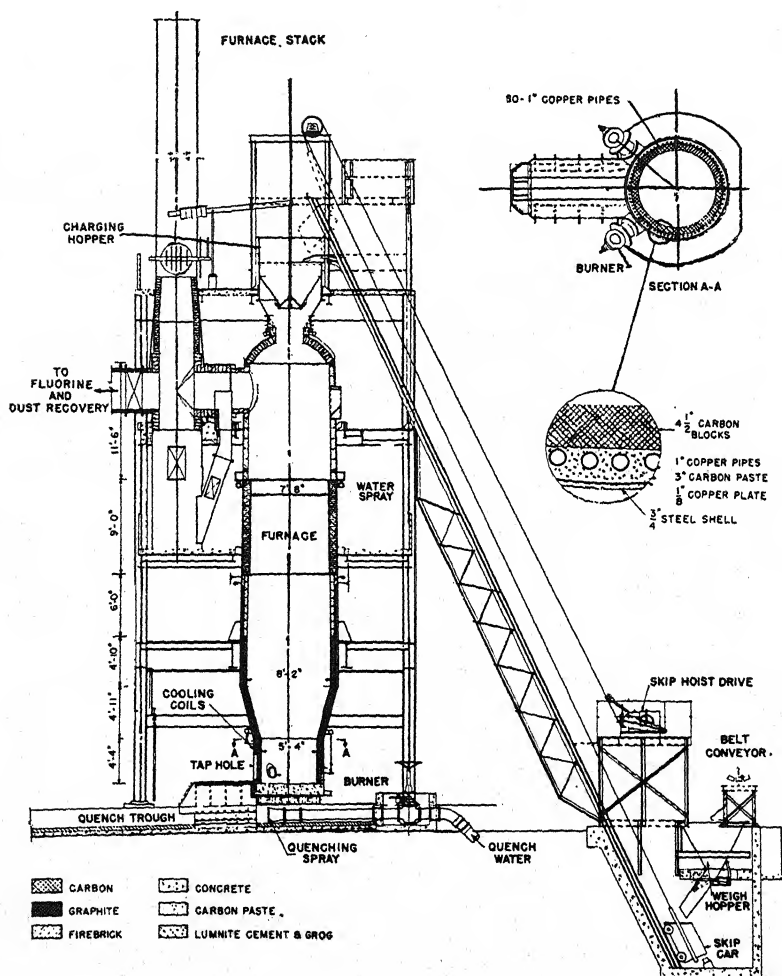
FIGURE 4. Cross-sectional sketch of one of the TVA's fused tricalcium phosphate furnaces near Columbia, Tennessee.

oil and 70,000 cubic feet of air are required per ton of product. Each ton of product requires about 5 gallons of fuel oil for drying and about 3 gallons
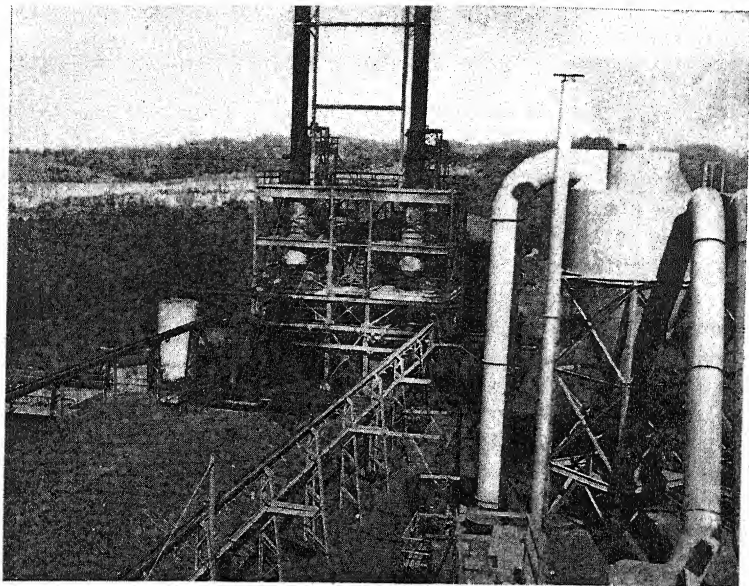
FIGURE 5. View of the two TVA fused tricalcium phosphate furnaces near Columbia, Tennessee. Product storage pile is in foreground.
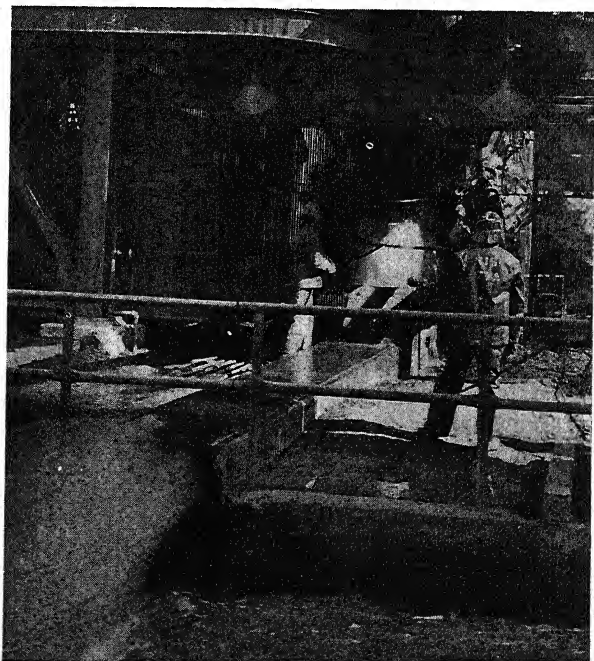
FIGURE 6. Tapping one of the TVA's fused tricalcium phosphate furnaces.

for generating steam for heating purposes. Other cost requirements per ton are 130 kw-hours for power, 4,000 gallons of water and 2.7 man hours of labor (based on full capacity of 150 tons per day). These figures do not include maintenance labor, administration, and operation of plant service facilities.

Fused tricalcium phosphate is described as a grayish-green material that does not cake, is non-hygroscopic, and is insoluble in water.

Examination of the quenched material shows alpha tricalcium phosphate, glass, and cristobalite[26]. It contains from 26 to 30 per cent total P_2O_5, 38 to 42 per cent CaO, 20 to 25 per cent SiO_2, 7 to 12 per cent Fe_2O_3 + Al_2O_3, and 0.2 to 0.4 per cent fluorine. About 80 per cent of the P_2O_5 is soluble in 2 per cent citric acid by the Wagner method, and about 75 per cent is soluble in neutral ammonium citrate. The laboratory tests do not give as good results as those obtained from crop responses in certain field plot tests[26].

The finished product is distributed on a basis of the total P_2O_5 present and 0.4 per cent maximum fluorine content. It is claimed that this is a better indicator of its value as a plant food than other chemical methods employed[26]. Extensive feeding tests have demonstrated the value of fused tricalcium phosphate as a source of phosphorus and calcium when added as a supplement to animal feeds[17].

Recovery of Fluorine

An outstanding development in connection with the processing of phosphate rock to produce fused tricalcium phosphate is the recovery of fluorine.

The recovery process according to a recent article by Hignett and Siegal[27] consists of removing dust from the stack gases and absorbing fluorine as HF in a bed of lump limestone at temperatures above the dew point of the stack gases. Studies indicated that a temperature range of 200 to 900°F (93 to 482°C) was satisfactory for fluorine absorption. Portions of the limestone are removed from the tower at intervals and the fines, which contain from 80 to 95 per cent CaF_2 are screened out. The oversize lumps, which are partially reacted, are returned to the tower with additional fresh limestone. "Fluorine recovery in the pilot plant, using a 4-foot bed of limestone, was as high as 96 per cent for extended periods." It was calculated that practically complete recovery can be made by increasing the depth of limestone in the tower to about nine feet. Recovery is largely governed by the rate of removal of the reaction product. No corrosion problems were experienced in 25 weeks operation of the pilot plant, the absorption tower of which was constructed of steel. The process and equipment are relatively simple, and there are no operating variables requiring close control. Lime

stone of a suitable size can be purchased at \$1.00 to \$2.00 per ton at the quarry[27]. A large-scale unit near Columbia, Tennessee, is in operation and is satisfactorily recovering fluorine from the furnace gases as calcium fluoride of a commercial grade.
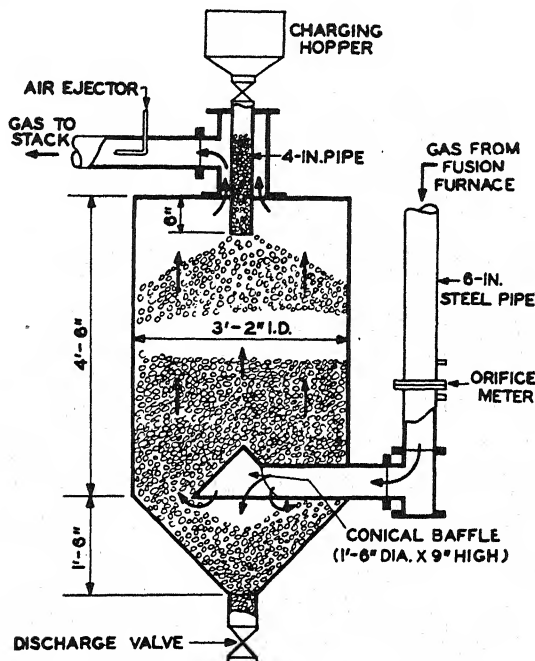
FIGURE 7. Pilot-plant tower for absorption of fluorine in lump limestone. [T. P. Hignett and M. R. Siegel, Tennessee Valley Authority, *Ind. Eng. Chem.*, **41**, 2494 (1949).]

PRODUCTION OF DEFLUORINATED PHOSPHATE ROCK IN ROTARY KILNS

After extensive experimental work it was found that substantially complete defluorination could be accomplished without fusion by addition to the phosphate rock of a proportion of silica greatly in excess of that normally contained in the rock. In general, the calcining charge should contain in excess of 35 per cent silica, and in the case of rock used at Coronet the proportion of silica should approximate 45 per cent. The process was first carried out by the Coronet Phosphate Co. in the laboratory by subjecting the charge to intimate contact with water vapor at a temperature in excess of 2600°F (1427°C). It was developed in successive steps from the laboratory to a 20″ x 8′ pilot kiln and finally to a 8′ x 140′ rotary kiln[39]. Operations

on a production basis were first conducted in a cement plant of the Valley Forge Cement Company at West Conshohocken, Pennsylvania. A plant was later constructed by the Coronet Phosphate Company near their mines at Plant City, Florida, where defluorinated phosphate is now being produced on a commercial scale.

The raw material used is a mixture of ground phosphate and ground sand (flotation tailings or flotation heads) blended to give the desired ratio of phosphate and silica[61].

The flow sheet of the plant is shown in Figure 8.   Phosphate concentrates

1   RAW MATERIALS STORAGE
2   TUBE MILL
3   SLURRY PUMP
4   SLURRY TANKS WITH MIXERS
5   SLURRY FEED PUMP
6   FEED TANK
7   FERRIS WHEEL FEEDER
8   ROTARY KILN
9   DRAG CONVEYOR
10   ELEVATOR
11   CLINKER STORAGE
12   ROLLER MILL
13   SCREW CONVEYOR
14   FULLER KINYON PUMP
15   FINISHED PRODUCT STORAGE
16   ROTARY FEEDER
17   SCREW CONVEYOR
18   ELEVATOR
19 BAGGING
20 LOADING
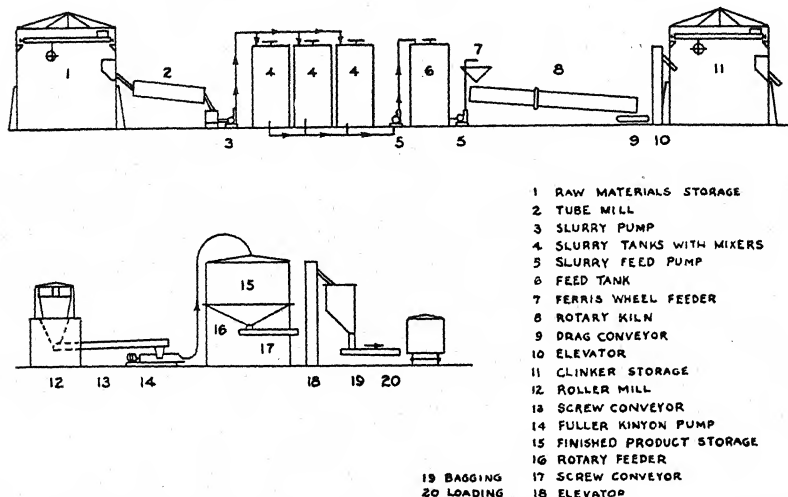
FIGURE 8. Flow sheet of defluorinating plant. [W. T. Whitney & C. A. Hollingsworth, *Ind. Eng. Chem.*, **41**, 1325 (1949).]

and tailings (or flotation heads) are hauled from the mines in hopper-bottom cars and dumped in separate piles on the raw material storage in craneway. The concentrates analyze about 34 to 35 per cent P_2O_5 and the tailings about 90 per cent SiO_2. Phosphate and sand are usually ground separately. The raw material is picked up from storage by a P & H (Harnischfeger Corporation, Milwaukee, Wisconsin) electric overhead crane having a bucket capacity of 2.125 yards and dumped into a 75-ton feed hopper. It is then fed by a table feeder to a 7 x 35 foot Traylor tube mill. Water is added to the feed to form a slurry containing from 35 to 45 per cent water. The material is ground to about 85 per cent through a 200-mesh screen.

The slurry from the mill is discharged into a tube and pumped by a centrifugal pump to one of the Dorr slurry mixers. There are seven of these

mixers, 20 feet high and 15 feet in diameter. Two are usually used for phosphate, two for sand, two for blending, and one for the kiln feed. They are equipped with mechanisms consisting of revolving arms driven by motors and aerating pipes through which compressed air is forced for continuous agitation.

The raw materials are blended and fed to the kiln in the form of a slurry contains from 42 to 45 per cent silica on the dry basis, and 40 to 45 per cent water according to the nature of the material being treated. The slurry is pumped from feed tank to ferris wheel feeders which discharge
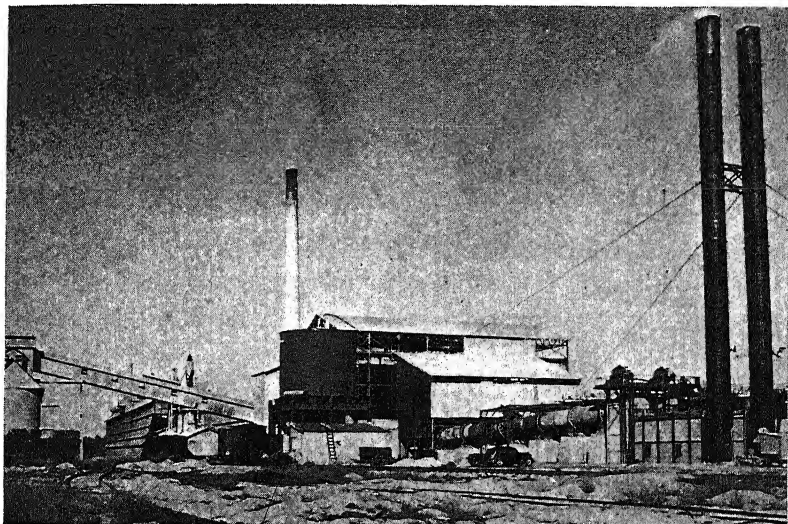
FIGURE 9. Production of defluorinated phosphate rock near Plant City, Florida.

into the kilns. The overflow from the feeder is returned to the kiln feed tank. The feeder is driven by a variable speed motor and speed reducer. The rate of feed is controlled at the firing end of the kiln.

Two kilns 6 feet 6 inches in diameter and 135 feet long are now in operation. They are driven by 25-h-p variable speed, direct current motors with a variation in speed from 66 to 108 seconds per revolution. Firing is by specially designed oil burners using Bunker C oil with steam for atomization. About 60 pounds of oil pressure, 55 to 60 pounds of steam, and an oil temperature of 175°F (79°C) are normally used. The load is quenched just before being discharged from the kiln by jets of water. This produces the excess of water vapor necessary for effective defluorination. The rapid cooling of the clinker prevents *alpha* tricalcium phosphate formed at de-
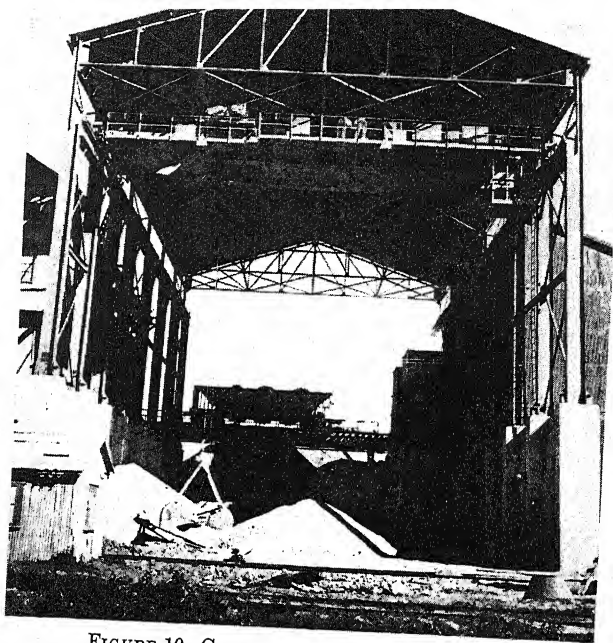
FIGURE 10. Craneway raw material storage.
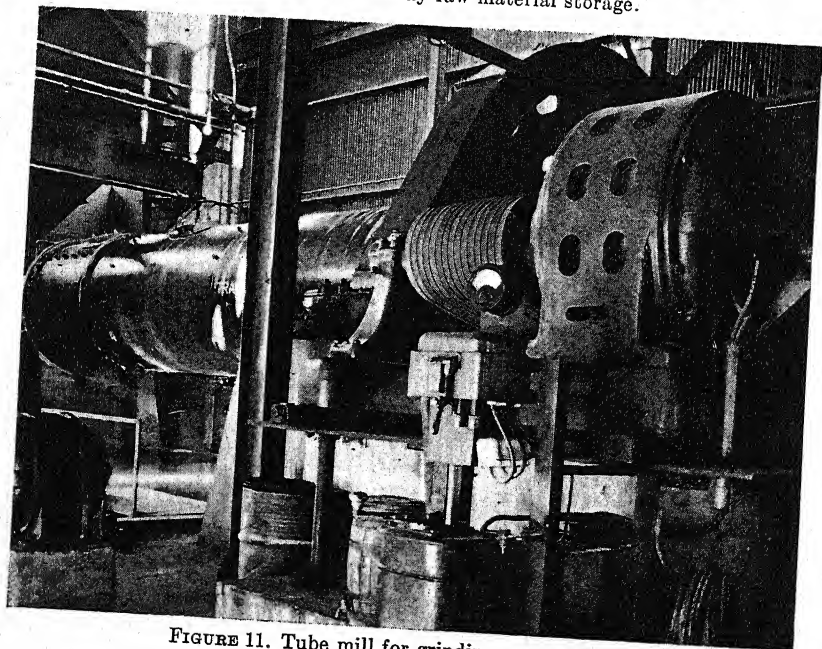
FIGURE 11. Tube mill for grinding raw material.

fluorinating temperatures from reverting to the *beta* form with its lower availability.

The temperature of the load in the burning zone is 2700 to 2900°F (1482 to 1593°C). The increase of temperature of the load is gradual and is controlled by regulation of flame and speed of kiln. The burning zone is approximately 30 feet in length and the load remains in this zone from 20 to 30 minutes. The temperature at the feed end varies between 1000 and 1400°F (538 and 760°C), according to the rate of feed, the content of water, and other operating conditions. Temperature readings and recordings are taken on the load at the firing end of the kiln by means of an optical pyrometer and a Leeds & Northrup Rayotube connected with an indicator and a recording chart placed on the firing floor.

The refractory lining of the kilns consists of 80 feet of 6-inch 70 per cent alumina brick in the hot end. The balance of the kiln is lined with 6-inch super duty brick, including the nose ring block and 4 feet next to the discharge end. There is no apparent reaction of the volatilized fluorine compound with the refractory lining of the kilns or stacks.

The clinker discharged from the kilns is conveyed to storage and then transferred to a 65-ton feed hopper, from which it is fed to a Bradley Hercules roller mill by a table feeder and ground to a fineness of approximately 60 per cent through 200-mesh. The product is then bagged and loaded into cars for shipment.

Laboratory control is necessary from the grinding of the raw materials to bagging the finished product. Adjustment of the burning operation is controlled by the fluorine content of the clinker.

The product as discharged from the kilns is in the form of nodules of a grayish green color closely resembling cement clinker. Nodules vary in size from $\frac{1}{16}$ to $\frac{1}{2}$ inch in diameter. The ground material is free flowing, non-hygroscopic, non-acid, and insoluble in water.

The following are typical analyses of Coronet defluorinated phosphate:

	(1) (%)	(2) (%)	(3) (%)
P_2O_5 Total	20.55	21.01	20.59
P_2O_5 Available 0.4% HCl	19.86	20.56	20.34
P_2O_5 Available 2% citric acid	19.56	19.83	19.14
P_2O_5 Available neutral ammonium citrate	18.58	18.01	18.59
CaO	28.80	28.77	28.58
Fe_2O_3	0.87	0.83	1.03
Al_2O_3	0.76	0.71	0.65
F	0.02	0.06	0.08[61]
Insoluble siliceous matter	48.65	47.64	48.20

Examination of Product

At present the solubility in 0.4 per cent of hydrochloric acid is used to evaluate available phosphorus for feeding purposes. The official ammonium citrate method is the standard for estimating available phosphorus for plant food. The Wagner method with 2 per cent citric acid is also used. The proportion of available phosphorus in relation to the amount of fluorine removed shows a rather flat curve until the greater part of the fluorine has been eliminated, after which the curve rises sharply. Therefore, the fluorine content is an indication of the phosphorus availability of the product for either animal or plant consumption.

The original form of the silica is quartz, which at the temperatures used in this process is almost entirely converted to cristobalite, a form of silica which melts at temperatures in excess of 3000°F (1649°C)[61].

Examination of the structure of the material by microscopic and x-ray diffraction methods identifies the phosphate constituent as *alpha* tricalcium phosphate. It is characterized by relatively large amounts of cristobalite and small amounts of glass.

The material, being substantially free from fluorine, is a non-toxic source of calcium and phosphorus for stock and poultry feeds. Nutrition experiments have demonstrated that the phosphorus and calcium in the product are readily utilized and compare favorably with pure *alpha* tricalcium phosphate and bone meal[17].

Plant growth experiments conducted by the Bureau of Plant Industry, U. S. Department of Agriculture, show that under certain conditions defluorinated phosphate rock has the same plant food value as superphosphate per unit of phosphorus pentoxide[1].

Methods for fluorine recovery are being studied. For the time being, flue gases containing fluorine are neutralized by blowing pulverized limestone into the bases of the stacks[61]. Plans have been made and changes are being instituted to improve both the process and the product.

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21. Calcium and Potassium Metaphosphates and Miscellaneous Products

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The two compounds of metaphosphoric acid that offer the greatest promise from an agricultural standpoint are calcium and potassium metaphosphates. The chief advantage that these products possess over superphosphate, basic slag and certain other phosphatic fertilizers is their high content of plant food which renders them economical to handle, ship and distribute.

Metaphosphates can be readily produced by any one of the three methods illustrated by the following typical reactions:

(1) Dehydration of monobasic orthophosphates at moderate temperatures.

$$CaH_4(PO_4)2 \cdot H_2O \rightarrow Ca(PO_3)_2 + 3H_2O$$
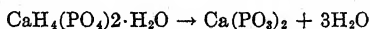
(2) Addition of phosphorus pentoxide to tribasic or dibasic orthophosphates at elevated temperatures.

$$Ca_3(PO_4)_2 + 2P_2O_5 \rightarrow 3Ca(PO_3)_2$$

(3) Decomposition of chlorides with phosphoric acid and volatilization of the resultant HCl and water at elevated temperatures.

$$KCl + H_3PO_4 \rightarrow KPO_3 + HCl + H_2O$$

The first method may be carried out at relatively low temperatures (275 to 300°C). Methods 2 and 3, however, involve temperatures ranging from 800 to 1200°C and the production of fused products.

Although virtually insoluble in water, the high solubility of calcium and potassium metaphosphates in neutral ammonium citrate solution and several other solvents is considered a strong indication of their agricultural availability. Moreover, in field and pot experiments where these products have been applied on certain types of soils, substantial increases in crop yields have been obtained.

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Calcium Metaphosphate

Whereas, the idea of producing calcium metaphosphate by the action of P_2O_5 on phosphate rock was covered by a patent issued to Pristoupil in Germany in 1930 and by two U. S. Patents issued to the same inventor[31] in 1930, little attention was paid to this invention until 1935 when the Tennessee Valley Authority independently discovered the fundamental principles involved and recognized the potentialities of such a product[11, 12].

In order to protect the interests of the American people and permit the further development of this process, the patents were purchased from the original inventor and intensive investigations conducted to determine the most practicable type of equipment to use and the optimum conditions required for the manufacture of this product.

The temperature best adapted for this reaction ranges from 1000 to 1200°C or several hundred degrees less than that required to fuse phosphate rock. The resultant product is tapped from the furnace as a syrupy liquid which hardens on cooling to a glass-like slag.

The ratio of P_2O_5 to CaO in calcium metaphosphate is 3 to 1 as against only 1 to 1 in phosphate rock. Since it contains neither water of crystallization nor constitution it has a higher percentage of phosphorus than any other phosphate fertilizer. The concentration of pure calcium metaphosphate in terms of P_2O_5 is 71.7 per cent but the commercial grades seldom contain more than 64 per cent due to the impurities in the phosphate rock used in its manufacture. The presence of such impurities as silica, iron and alumina render the composition of the final product somewhat complex[18]; high percentages of iron and alumina are undesirable but their deleterious effect on the solubility of the product is usually counteracted by the silica present.

Although calcium metaphosphate is not water-soluble, it may be regarded as derived from readily soluble monocalcium phosphate which has been completely dehydrated. Under favorable conditions it will take up water and form monocalcium phosphate. Frear *et al.*[18] found that autoclaving this compound at 180°C with a small amount of water converted it into monocalcium phosphate and that the metaphosphate also gradually dissolved in rain water. Ordinarily this conversion to a water-soluble form is a slow process and as a result the agricultural value of calcium metaphosphate is based on its solubility in a neutral solution of ammonium citrate.

Manufacture of Calcium Metaphosphate

The manufacture of calcium metaphosphate on a commercial scale is dependent upon P_2O_5 derived from the combustion of phosphorus and is only practicable where the thermal reduction method for the production of this element is employed. One of the main advantages of the metaphosphate

process lies in the fact that the P_2O_5 derived from the combustion of phosphorus is made to react directly on mineral phosphates instead of being first converted into phosphoric acid and this acid subsequently used to decompose phosphate rock. It is obvious therefore that at least one processing step can thus be eliminated[12, 13].

Theoretically the manufacture of calcium metaphosphate is relatively simple, but in adapting this process to commercial practice, certain physical and chemical problems developed which have not yet been entirely solved, and further investigations are required to effect the maximum economies and establish the conditions under which this product is most effective as a fertilizer material.

So far, two modifications of the calcium metaphosphate process have been tried on a small commercial scale by the TVA. The first modification consists in burning elemental phosphorus in a combustion chamber which leads into the base of a shaft furnace containing lump or nodular phosphate rock. In starting up the plant the furnace is heated by an oil flame until a temperature of 1000°C is reached. The phosphorus burner is then turned on and the heat of combustion of this element is more than sufficient to carry on the desired reactions without auxiliary fuel. The hot P_2O_5 in passing through the column of stock reacts with the phosphate rock to produce calcium metaphosphate which melts and flows down the shaft where it is collected in a pool provided for the purpose. The impurities in the phosphate rock dissolve in or combine with the metaphosphate which is periodically tapped off as a molten slag. The product may be quenched with water or air-cooled, crushed, finely ground and sacked. As the stock in the shaft melts, further quantities of phosphate rock are added through a suitable feeding device near the top of the furnace. The residual gases substantially free from P_2O_5 are discharged from the furnace and may be passed through scrubbing equipment to remove or collect the fluorine products.

Maintenance of the proper temperature in the furnace is highly important in order to render this process continuous and insure complete absorption of the P_2O_5. Whereas hot P_2O_5 will combine readily with phosphate rock, it is necessary that the temperature of the furnace be sufficiently high to melt the coating of calcium metaphosphate formed on the rock and thus expose fresh surfaces of the latter to the action of the hot gases[17]. It is also necessary to provide means for preventing the phosphate rock in the furnace shaft from falling into the molten pool of calcium metaphosphate, thus diluting the product with material that has not been acted upon.

Several schemes have been devised to overcome this difficulty but the most practicable arrangement appears to be a grate or refractory platform a short distance below the mouth of the furnace shaft which will support

the column of stock, yet permit the passage of the combustion products through the furnace shaft. The various stages in the development of this type of furnace as described by Curtis et al.[13] are shown in Figure 1.

One of the main problems encountered in the manufacture of calcium metaphosphate has been that of obtaining suitable refractories which will stand up under the severe conditions imposed upon them[30]. All siliceous or basic refractories so far used are attacked by P_2O_5 or molten metaphosphate at high temperatures and dissolve in the slag-like product.

By externally cooling the furnace shell the life of the refractory lining can be greatly prolonged since an equilibrium is established which maintains a certain thickness of furnace wall even though this lining may even-
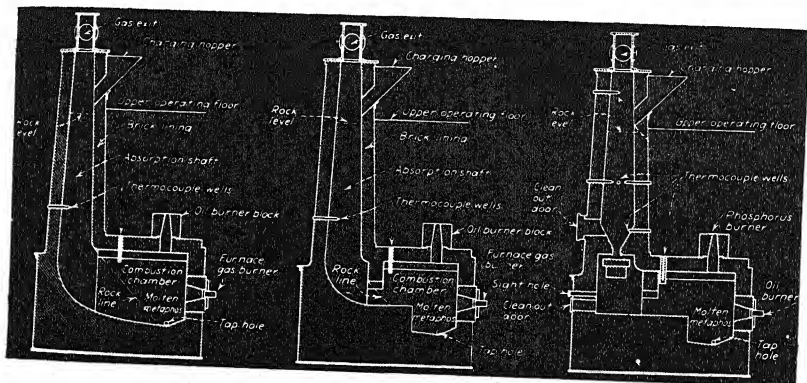
(Courtesy of TVA)

FIGURE 1. Development of the calcium metaphosphate furnace by the Tennessee Valley Authority. The figure on the right shows the latest type employed.

tually consist largely of congealed metaphosphate. However, the maintenance of the grate or platform for supporting the phosphate charge in the furnace where the temperature is at a maximum is still a major problem.

Numerous types of refractories have been tried as well as such devices as water- or air-cooled pipes protected by graphite sleeves and covered with refractory cement. None of these have proved entirely satisfactory although they have prolonged the life of the combustion chamber and the lower part of the furnace shaft permitting campaigns of reasonable length without major repairs.

Another problem in the manufacture of metaphosphate has been that of maintaining a proper ratio between the CaO and P_2O_5 so that the maximum citrate solubility is attained without forming a hygroscopic product. Curtis and his co-workers[13, 14] state that if crude calcium metaphosphate is to be used as a fertilizer the molecular ratio of P_2O_5 to CaO

in the product should be held as near unity as possible. When the proportion of P_2O_5 is increased much beyond this point, the product is hygroscopic and tends to cake when finely ground and exposed to a humid atmosphere. This hygroscopicity however can be largely overcome by the addition of finely ground limestone[18, 28].

Composition

A typical analysis of calcium metaphosphate prepared from Tennessee brown rock phosphate according to the process just described is as follows:

	(%)
Silica (SiO_2)	4.3
Lime (CaO)	24.5
Phosphoric acid (P_2O_5)	64.6
Iron and alumina (Fe_2O_3, Al_2O_3)	3.7
Fluorine (F)	0.2

A modified plant for the manufacture of calcium metaphosphate was designed by TVA with a view to obviating the necessity of providing a supporting column for the furnace stock. In this plant finely ground phosphate rock was sprayed into the phosphorus combustion chamber and any excess of P_2O_5 that failed to combine therewith was absorbed by phosphoric acid that percolated down through a column of lump coke contained in a shaft surmounting the combustion chamber. The coke in this shaft was supported by a water-cooled grate protected from direct contact with the products of combustion.

On account of the comparatively lightweight of this coke column and the cooling action of the percolating phosphoric acid, the strain on the supporting grate was much less than where the shaft was packed with heavy lumps of phosphate rock and higher temperatures were attained at the mouth of the furnace shaft.

Other problems, however, developed when using this type of furnace such as difficulty in keeping the finely ground unreacted rock from blowing up through the column of coke, and maintaining the proper balance between the reacting materials necessary for manufacturing a uniform product. This furnace was altered a number of times but did not prove very satisfactory and eventually was converted into a phosphoric acid plant.

POTASSIUM METAPHOSPHATE

From the standpoint of concentration and the attendent economies in handling, shipping and distribution, potassium metaphosphate offers more attractive possibilities than any other fertilizer material. This compound when pure contains the equivalent of 39.87 per cent K_2O and 60.13 per cent of P_2O_5 and is the only product known composed of 100 per cent of plant-food ingredients.

So far this product has not been manufactured on a commercial scale but laboratory and semi-works experiments indicate that it may well play a highly important role in future fertilizer practice.

Potassium metaphosphate may be prepared in a number of ways but the most practical and promising method appears to be that based on the decomposition of potassium chloride with orthophosphoric acid at elevated temperatures and thus driving off both water and hydrochloric acid as shown below in equation (3).

A large proportion of the potash salts produced in this country and abroad is in the form of chloride and hence this compound is the logical raw material to use in the manufacture of potassium metaphosphate. Moreover, the hydrochloric acid which may be recovered as a by-product can be utilized in manufacturing other industrial products.

Ross[33] studied the reactions between phosphoric acid and potassium chloride up to temperatures of 250°C and Hazen and Ross[20, 34] obtained patents on the process which they developed. These inventors, however, used an excess of phosphoric acid to insure complete volatilization of the hydrochloric acid and avoided the formation of potassium metaphosphate by keeping the temperature of the reaction relatively low. The excess of phosphoric acid in the product was later neutralized with ammonia in order to obtain a compound containing the three fertilizer elements (N, P_2O_5 and K_2O) as described in Chapter 18. Some years later, however, Urbain[37] was issued a patent covering the manufacture of potassium metaphosphate by heating a mixture of KCl and H_3PO_4 to dull redness.

Manufacture of Potassium Metaphosphate

Madorsky and Clark[29] studied the formation of potassium metaphosphate produced by the reaction between phosphoric acid and potassium chloride over a temperature range of 300 to 900°C and have investigated the properties of the resultant products. The sequence of the main reactions involved may be briefly described as follows:

When molecular proportions of potassium chloride and phosphoric acid are mixed and heated, both water and hydrochloric acid are evolved. The loss of water results first from the concentration of the orthophosphoric acid, second from the conversion of phosphoric acid into pyrophosphoric acid and finally, from the dehydration of pyrophosphoric acid and its conversion into metaphosphoric acid. Monopotassium phosphate, potassium acid pyrophosphate and potassium metaphosphate are produced successively as shown in the following equations:

$$2KCl + 2H_3PO_4 \rightarrow 2KH_2PO_4 + 2HCl \tag{1}$$

$$2KH_2PO_4 + heat \rightarrow K_2H_2P_2O_7 + H_2O \tag{2}$$

$$K_2H_2P_2O_7 + heat \rightarrow 2KPO_3 + H_2O \tag{3}$$
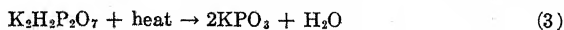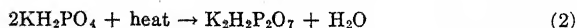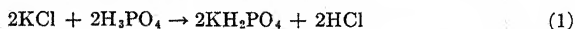
The final traces of HCl probably are not driven off until the potash has been completely converted into metaphosphate.

If an excess of potassium chloride is used in this process the product contains appreciable quantities of normal potassium pyrophosphate as indicated in the following equation:

$$4KCl + 2H_3PO_4 \rightarrow K_4P_2O_7 + 4HCl + H_2O$$

In most cases Madorsky and Clark[29] used equi-molecular proportions of phosphoric acid and potassium chloride to insure the maximum proportion of metaphosphate in the product. The composition of the reaction products obtained by these investigators at various temperatures is given in part in Table 1.

Potassium metaphosphate prepared in this way at temperatures ranging from 700 to 900°C is virtually insoluble in water, but its P_2O_5 content is soluble in boiling ammonium oxalate solutions when tested according to official methods for fertilizer materials[1].

The melting point of pure potassium metaphosphate is approximately 807°C or 170 degrees lower than that of calcium metaphosphate. The product should therefore have a somewhat less scorifying action on furnace refractories at this lower temperature. Unlike calcium metaphosphate, which forms a glassy product, fused potassium metaphosphate when cooled has a definite crystalline structure.

In addition to the process described above, the Tennessee Valley Authority has produced potassium metaphosphate on a pilot-plant scale by two modifications of their method for manufacturing calcium metaphosphate[10].

In the first series of experiments it was attempted to take advantage of the low-melting point of potassium chloride by fusing the salt in an electric furnace and permitting it to flow down a shaft furnace (packed with refractory material), countercurrent to an upward stream of gas containing P_2O_5 derived from the burning of phosphorus with moist air in an auxiliary combustion chamber. This method, however, entailed a number of mechanical and chemical difficulties such as the solidification of the potassium chloride as it flowed into the upper part of the furnace and the incomplete reaction between the P_2O_5 and the potash salt. To overcome these objections the upper part of the furnace was then operated at a temperature considerably above the melting point of potassium chloride. Under such conditions however substantial proportions of both potash and phosphoric anhydride were volatilized and carried out of the furnace along with the hydrochloric acid, and the corrosive nature of the products at these higher temperatures vigorously attacked the refractory packing of the tower. Only zircon withstood the scorifying action of these products.

In the second series of experiments potassium chloride was finely ground

TABLE 1. COMPOSITION OF REACTION PRODUCTS OF POTASSIUM CHLORIDE-PHOSPHORIC ACID MIXTURES[a]

Reaction Mixt.				Observed Analysis of Product									Equivalent Analysis of Composite Product					
Max. Temp. (°C)	Initial ratio KCl/H₃PO₄	Volatilization loss	Insol. fraction, K₃PO₄	Soluble fraction									K₂O	P₂O₅	Cl₂	H₂O[b]	H₂O[c]	Cl₂/P₂O₅
	Moles	Weight per cent		1st H⁺	2nd H⁺	3rd H⁺	K⁺	Cl⁻	PO₄⁻	P₄O₇----	PO₃⁻	Total	Weight per cent					Moles
300	1.00	28.43	0.274	0.207	0.436	0.276	28.61	6.04	26.69	12.33	25.99	100.85	34.57	53.65	6.04	7.10	8.21	0.225
350	1.00	32.30	45.58	0.127	0.226	0.146	15.61	3.65	12.17	7.87	13.72	99.10	36.97	55.02	3.65	5.18	4.46	0.133
400	1.00	34.44	69.59	0.095	0.126	0.075	8.62	3.47	9.80	1.21	7.04	100.03	38.13	56.90	3.47	2.28	2.65	0.122
500	1.00	35.23	75.11	0.073	0.081	0.078	6.98	2.86	6.48	1.50	7.33	100.49	38.36	57.68	2.86	1.75	2.07	0.099
500[d]	1.00	35.99	77.84	0.066	0.078	0.082	6.29	2.55	5.86	0.388	7.72	100.89	38.62	58.18	2.55	1.23	2.02	0.088
500	1.05	36.01	79.27	0.051	0.059	0.023	6.77	3.79	7.26	0.617	2.21	100.05	39.77	56.33	3.79	0.97	1.19	0.135
500	1.10	35.46	80.29	0.043	0.063	0.032	6.98	4.37	5.14	0.388	2.97	100.28	40.42	55.44	4.37	0.76	1.23	0.058
600	1.00	35.60	76.65	0.061	0.064	0.073	6.73	2.05	7.03	0.503	6.86	100.02	38.67	57.95	2.05	1.79	1.77	0.071
700	1.00	36.75	87.03	0.023	0.025	0.040	3.62	0.277	5.48	0.377	3.74	100.61	39.06	60.37	0.277	0.353	0.783	0.009
800	1.00	37.97	96.75	0.005	0.009	0.007	0.879	0.241	0.963	0.354	0.668	99.88	39.64	59.82	0.241	0.349	0.188	0.008
800	1.02	37.78	97.39	0.000	0.011	0.004	1.13	0.635	0.342	0.057	0.390	99.96	40.19	59.21	0.635	0.105	0.135	0.002
800	1.05	37.24	93.81	0.000	0.008	0.010	2.66	1.00	0.332	0.914	0.963	99.70	40.60	58.17	1.00	0.460	0.163	0.034
800	1.10	37.05	90.51	0.000	0.000	0.017	4.51	2.02	0.471	1.06	1.56	100.15	41.52	56.88	2.02	0.040	0.148	0.071
900	1.00	37.94	97.44	0.004	0.010	0.002	0.701	0.162	0.781	0.320	0.187	99.61	39.69	59.69	0.162	0.498	0.143	0.005

[a] Reaction mixtures gradually heated to and maintained at maximum temperature for 1 hour.
[b] By difference.
[c] Equivalent to 1st, 2nd, and 3rd hydrogens.
[d] Maintained at 500° C. for 2.5 hours.

(98 per cent -14 mesh) and blown into a reaction chamber adjacent to the phosphorus combustion chamber maintained at a temperature of 1000 to 1050°C, the P_2O_5 and K_2O being introduced in the proper proportions to form potassium metaphosphate. The shaft surmounting the reaction chamber was packed with coke down which water and recycled phosphoric acid percolated. The coke column was supported by a water-cooled grate which stood up fairly well due to the lower temperatures involved. Any P_2O_5 that did not combine with the fine spray of potash salts was absorbed by the water and phosphoric acid that percolated over the coke packing.

The gases left the packed tower at 100°C and passed to a cooler where their temperature was reduced to 70 to 80°C before entering the hydrochloric acid recovery system. The phosphoric acid recovered from the cooler was recycled to the packed tower. The molten product (potassium metaphosphate) collected in the bottom of the combustion chamber and was tapped every 2 hours into a water-cooled pan where it was allowed to solidify.

TABLE 2. OPERATING DATA (78-HOUR TEST) FOR THE POTASSIUM METAPHOSPHATE PILOT PLANT

Phosphorus (99.2% P_4) burned, tons/day	1.27
Potassium chloride (61.3% K_2O) charged, tons/day	2.64
Potassium metaphosphate (58% P_2O_5; 35% K_2O; 1.8% Cl) produced, tons/day	4.31
Recovery of phosphorus as potassium metaphosphate (%)	87.00
Recovery of potassium as potassium metaphosphate (%)	93.00
Volatilization of chlorine as HCl (%)	94.00

Operating Data

The operating data and results obtained in a 78-hour run during which 14 tons of potassium metaphosphate were produced are given in Table 2.

According to Curtis[12] these preliminary experiments have shown considerable promise, but the process was not developed to a point where it has been adapted to commercial practice.

MISCELLANEOUS AVAILABLE PHOSPHATES

Various other processes have been proposed for rendering phosphate rock available, but few, if any have been developed on a commercial scale. Some of those that have attracted attention are based on the gradual solubilizing of phosphate in the soil either by direct or indirect action of bacteria.

Bacterized, Sulfur-Bearing Phosphates

The fact that bacteria might increase the solubility of the P_2O_5 in bone meal was suggested by Stoklasa *et al.*[36] in 1900. Koch and Krober[20] also

found that a number of relatively insoluble phosphates were rendered soluble by the acids formed by sewage and soil bacteria. A number of other investigators, notably Sackett and his co-workers[35] and Bassalik[3], also reported that certain types of soil bacteria exert a solvent action upon mineral phosphates. Later Hopkins and Whiting[21] corroborated the results obtained by Bassalik, showing that the nitrous acid formed by nitrite bacteria rendered finely ground phosphate rock available.

The process of Coates[8] (who has a number of patents supplementary to that for bacterized phosphate[9]) consists in adding rock and breaking down bacteria to mineral phosphates which have been sterilized by heat treatment. It is claimed the bacteria continue to act upon the phosphate rock, rendering the phosphoric acid contained therein available to crops.

The mixing of sulfur with phosphate rock to render the latter available was proposed and patented by Chisolm[5] in 1905 and 1906. While little was said at that time regarding the oxidation of sulfur and the secondary effect thus produced upon the mineral phosphates, the formation of sulfuric acid in the soil by oxidation of sulfur was noticed as far back as 1869.

In 1915 Chisolm[6] took out another patent in which he claimed that soluble phosphate was obtained by intimately mixing and grinding together sulfur and phosphate rock and then introducing sufficient moisture to promote the formation of sulfuric acid.

Lipman's first patent[23] covers the mixing of sulfur and phosphate rock with soil, well rotted stable manure or other material carrying microorganisms which tend to oxidize the sulfur present. In his two subsequent patents[24] he claimed the production of a phosphate fertilizer by mixing phosphate rock, sulfur and sulfofying bacteria.

Experiments reported by Lipman, McLean and Lint[25] have shown that by composting phosphate rock and sulfur with sand or soil containing sulfofying bacteria, distinct increases in the solubility of the phosphoric acid are obtained largely because of the conversion of the sulfur into sulfuric acid and the action of this acid upon the phosphate mineral. Lipman does not claim to get water-soluble phosphate acid by this method, but citrate soluble, or so-called available P_2O_5.

Where phosphate rock (15 parts and sulfur 5 parts) was composted with a relatively large quantity of soil (100 parts), Lipman and Joffe[26] found over 82 per cent of the P_2O_5 was converted into a citrate-soluble form in about 20 weeks. But in the experiments of Ellett and Harris[16] where amounts of soil and phosphate rock were more nearly equal (but the ratio of sulfur-to-rock was the same as in Lipman's experiments) approximately 19 per cent of the P_2O_5 present was rendered citrate soluble even after the compost heap had stood for 2 years.

A number of pot and field experiments[27, 32] have been conducted with

phosphate-sulfur composts and favorable results reported. If such a treatment should prove effective in rendering phosphates available it would have certain advantages over the sulfuric acid process in that low-grade phosphates unfit for the manufacture of superphosphate could be readily employed. Another advantage claimed is that the P_2O_5 contained therein is rendered available at a rather slow but constant rate, corresponding in a measure to the rate which crops absorb this plant food from the soil under optimum conditions.

Other patents for rendering phosphate rock available by means of sulfur are based on effecting more intimate contact between the rock particles and this element. Bodrero[4], for instance, proposes to sublime the sulfur into a mass of finely divided phosphate while the latter is being continually agitated in a rotating drum, claiming that the sulfur coating on the rock particles is more readily attacked by microorganisms.

Claiborne and Peterson[7] proposed the manufacture of porous pellets either by spraying from 30 to 40 per cent of liquid sulfur on finely ground phosphate rock or mixing the two materials in these proportions and subsequently forming pellets that pass a 20-mesh screen. The inventors state that if the phosphate is heated to 100°C or higher before the molten sulfur is added some of the phosphate will be rendered immediately available.

Gilbert[19] later filed what is purported to be an improvement over the Claiborne-Peterson patent. This comprised adding to the molten sulfur an amount of sulfuric, phosphoric or nitric acid sufficient to dissolve therein, mixing the slightly acidified sulfur with finely ground phosphate rock and forming pellets from this mixture.

None of the sulphur-phosphate mixtures are being produced in commercial quantities for fertilizer purposes at the present time.

Colloidal and Peptized Phosphate

So-called colloidal or peptized phosphatic fertilizers and processes for producing them have been proposed from time to time. Plauson[29a], for instance, patented a method which consisted in grinding phosphate rock intensively in a large quantity of water containing a very small amount of an inorganic acid or an alkali. After standing from $1\frac{1}{2}$ to 2 hours the dilute solution is drawn off, the settled product dried, disintegrated and used for fertilizer purposes. The inventor claims that by conducting the process at elevated temperatures (90 to 95°C) conversion of the rock into a colloidal-like product is facilitated.

DeHaën[15] advocates the grinding of phosphate rock to a medium degree of fineness with a solution of the putrifaction or decomposition products of vegetable fibers such as salts of lignin-acids or spent liquors from the manufacture of paper pulp. These, he claims, act as peptizing agents and cause

the colloidal dispersion of the phosphate. The slimes are separated from the coarser material and used for fertilizer purposes.

A series of patents have been issued to Bancroft *et al.*[2] covering phosphatic fertilizers obtained by adding certain amines to finely ground phosphate rock in amounts ranging from 1 to 10 per cent of the weight of the rock. These investigators state that insoluble P_2O_5 of the rock is thus released to crops, producing yields considerably in excess of those obtained when inorganic nitrates, ammonium sulfate and other common nitrogen carriers are used. Whereas the inventors do not claim a direct chemical reaction between the phosphate rock and the amines, they say the latter compounds cause a colloidal dispersion of the finely ground phosphatic material, and these so-called peptized particles supply the soil solution at a rate that has a marked effect on plant growth. The alleged advantage of this type of product is that it retains its availability after application under varying weather and soil conditions.

Phosphate fertilizers of this nature however cannot be evaluated by laboratory methods and their effectiveness must be demonstrated by carefully conducted field and greenhouse experiments before they are generally accepted.

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22. Complete Fertilizers and Their Preparation

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INTRODUCTION

The preparation of modern complete fertilizers imposes a number of problems to which little attention was given in the early days of the fertilizer industry. These problems are as follows:

(1) Physical and chemical nature of the various fertilizer ingredients employed.
(2) Chemical reactions involved when the various materials are mixed.
(3) Chemical and physical nature of the blend or mixture.
(4) Means for preventing caking and segregation of the various materials in the final product.

Before development of the concentrated fertilizer materials, the complete products on the market were of relatively low grade, many containing only 12 per cent of the plant-food ingredients N, P_2O_5 and K_2O. These mixed goods contained many low-analysis raw materials such as low-grade superphosphate (14 per cent P_2O_5), unrefined potash salts and organic by-products (cottonseed meal, fish scrap, and animal and garbage tankage). Probably ammonium sulfate (20 per cent N) and potassium chloride (63 per cent K_2O) were the most highly concentrated fertilizer materials generally available for a long period of time.

Large tonnages of sand and low-grade organics were used as fillers or conditioners in making up definite fertilizer formulas to prevent the final product from caking or setting and thus preventing its ready distribution in the field.

The undesirable chemical changes recognized by the manufacturer of mixed goods 30 or 40 years ago, and which he endeavored to avoid, were reactions that caused the reversion of P_2O_5 to an insoluble form and those that resulted in the loss of valuable nitrogen products through volatilization. It was known, for instance, that the addition of basic materials such as lime or limestone reduced the solubility of the P_2O_5 in superphosphate and caused loss of ammonia from ammonium sulfate. It was also

recognized that the addition of excessive quantities of nitrate of soda to mixtures containing superphosphate caused the evolution of valuable oxides of nitrogen and accelerated rotting of the fertilizer bags. Maintenance of the physical conditions of the finished goods however was not a major problem in these low-grade fertilizers because of the large percentage of organic or neutral filler which they contained.

Multiplicity of Formulas

In the early days of the fertilizer industry, and in fact up to 25 years ago, there was a tendency to produce a multiplicity of complete fertilizer mixtures. This was due in part to the keen competition in the fertilizer industry and the desire of the individual manufacturer to stress the virtues of his own particular brands. Unwarranted claims were made for blends of unusual composition made up from a wide variety of raw materials.

Certain consumers in turn specified special mixtures containing definite proportions of nitrogen from ammonium salts, nitrates and organic sources. Others were guided in their purchase of fertilizer by its color, odor and the size of the bag carrying a definite weight of the product.

Although the number of possible formulas (in terms of percentages of N, P_2O_5 and K_2O) was much less before the advent of concentrated fertilizer materials, many brands were offered which sometimes differed by fractions of a per cent of plant food.

These intricate mixtures and multiplicity of formulas complicated the manufacture of mixed fertilizers, added to labor and processing costs and increased the price of the product to the ultimate consumer.

Trend Towards Concentrated Fertilizers

Within the past 25 years there has been an ever increasing trend toward the manufacture and use of concentrated complete fertilizers. This has been due to a number of fundamental factors:

(1) The diversion of high priced and relatively low-grade organics (formerly employed in mixed fertilizers) to stock feeds wherein the nitrogen content in the form of protein is more efficiently utilized[5].

(2) The substantial rise in freight rates that have rendered transportation of plant food in low-grade products over long distances increasingly expensive[3, 13].

(3) The increase in the cost of labor that has forced the farmer to employ time-saving mechanized equipment and fertilizer products requiring a minimum of handling in their distribution.

(4) Technological developments which have made the production of concentrates economically feasible and converted a somewhat pre-

carious fertilizer business into an industry based on sound chemical and engineering principles[4].

This evolution in fertilizer manufacture does not mean that certain raw materials, the effectiveness of which has been definitely established, are no longer employed, but these have been supplemented by and reinforced with chemical compounds having such high concentrations that it is pos-
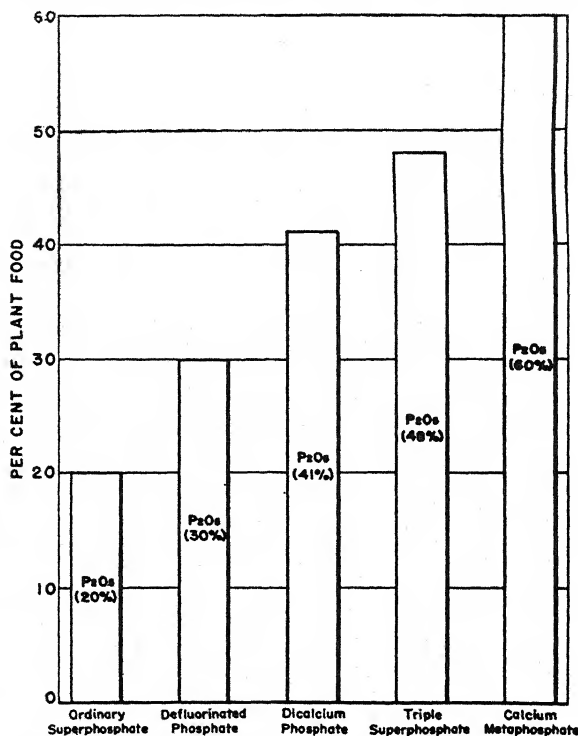
FIGURE 1. Manufactured phosphates containing only one fertilizer ingredient.

sible to raise the grade of the final products considerably above that of fertilizers previously used. According to Jacob[6] and Scholl and Wallace[12] the average plant-food content of mixed fertilizers has risen from 12 per cent prior to 1900 to 22.5 per cent in 1949.

Complete concentrated fertilizers containing all three of the main plant food constituents (K_2O, P_2O_5, N) can be manufactured in the following three ways:

    (1) By mechanically mixing separately prepared materials each of which contains a single fertilizer ingredient.

(2) By blending materials containing one, two and three fertilizer ingredients.

(3) By actually manufacturing a blended product in which each particle is substantially of the same composition.

The development of so-called ammoniating solutions containing free
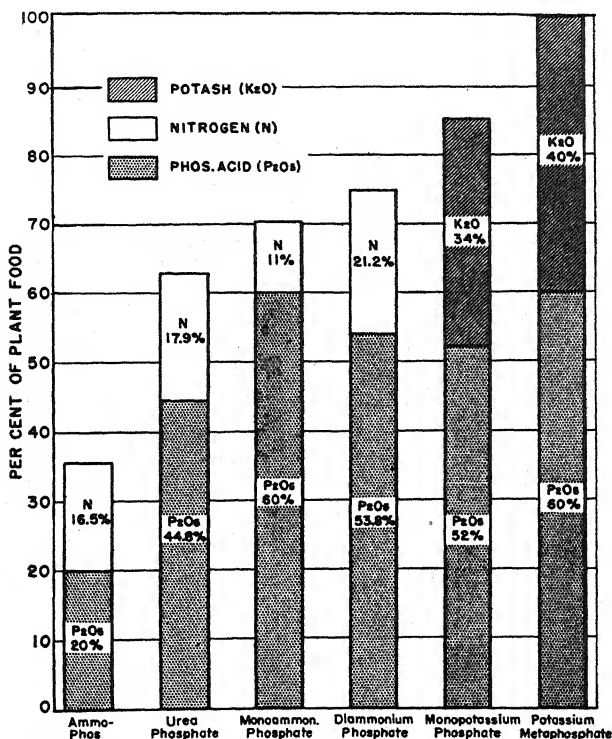
FIGURE 2. Manufactured phosphates containing two fertilizer ingredients.

ammonia and various soluble nitrogenous salts has contributed much to the manufacture of high analysis complete fertilizers.

The composition of manufactured phosphate products containing one, two and three fertilizer constituents that may be used in the preparation of complete fertilizers are shown in Figures 1, 2 and 3.

In addition to these phosphate carriers, the following chemical compounds and salts, commonly used in fetilizer mixtures contain potash,
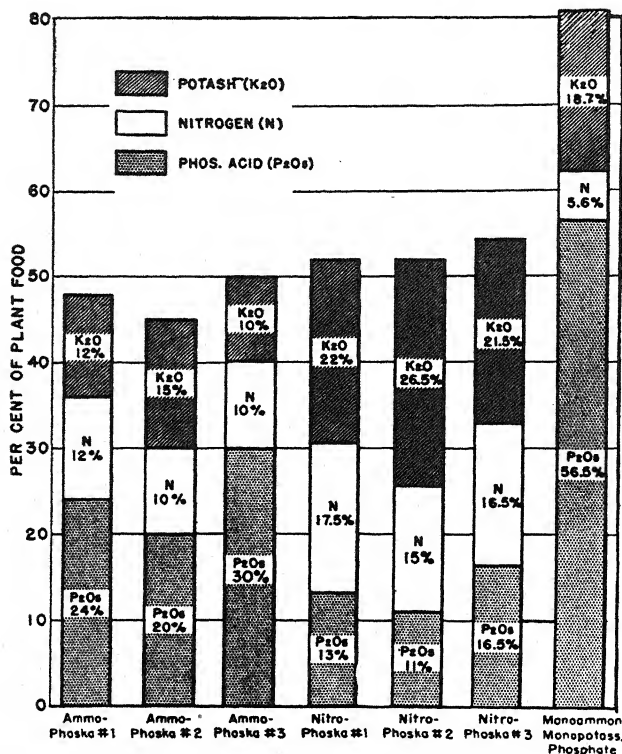
FIGURE 3. Manufactured phosphates containing three fertilizer ingredients.

nitrogen or both, but no phosphoric acid:

Nitrogen carriers
$\begin{cases} \text{Ammonium nitrate} \\ \text{Ammonium sulfate} \\ \text{Calcium nitrate} \\ \text{Cyanamide} \\ \text{Sodium nitrate} \\ \text{Urea} \end{cases}$

Potash carriers
$\begin{cases} \text{Potassium chloride} \\ \text{Potassium nitrate} \\ \text{Potassium sulfate} \end{cases}$

Preparation of Complete Goods from Simple Fertilizer Materials

When each fertilizer material employed contains a single plant food ingredient the quantities required in making up a specified fertilizer formula can be readily determined by means of simple equations as follows:

Let a, b and c represent the percentage of nitrogen (N), phosphoric acid (P_2O_5) and potash (K_2O) respectively in the three fertilizer materials.

Let A, B and C represent the percentages of these fertilizer ingredients desired in the complete goods.

Then the quantities (lbs) X, Y and Z of the three fertilizer materials required per ton of product are determined by substituting the known values in the following equations:

$$X = 2000\ \frac{A}{a}$$

$$Y = 2000\ \frac{B}{b}$$

$$Z = 2000\ \frac{C}{c}$$

After obtaining the quantities of X, Y and Z, the amount of filler (F) that must be added to make up a ton of the required formula is obtained from the equation:

$$F = 2000 - [X + Y + Z]$$

As a concrete example, it is assumed that a complete fertilizer having the formula 4 per cent N, 10 per cent P_2O_5 and 4 per cent K_2O is to be manufactured from raw materials having the following composition: Ammonium sulfate (20 per cent N), superphosphate (20 per cent P_2O_5) and potassium chloride (63 per cent K_2O). Substituting the known values in the equations given above we have:

$$X = 2000\ \frac{4}{20} = 400 \text{ lbs of ammonium sulfate}$$

$$Y = 2000\ \frac{10}{20} = 1000 \text{ lbs superphosphate}$$

$$Z = 2000\ \frac{4}{63} = 127 \text{ lbs potassium chloride}$$

$$F = 2000 - (400 + 1000 + 127) = \overline{473 \text{ lbs filler}}$$

$$\text{Total} = \overline{2000 \text{ lbs complete fertilizer (4–10–4)}}$$

It is obvious that the sum of $X + Y + Z$ cannot exceed 2000 pounds, which would make F a minus quantity. Therefore it is impossible to make high analysis complete fertilizers where only low or medium grade raw materials are available. For instance, a product analyzing 6 per cent N, 16 per cent P_2O_5 and 6 per cent K_2O could not be manufactured from ordinary superphosphate, ammonium sulfate and potassium chloride unless some concentrate such as triple superphosphate or ammonium phosphate were added.

Table 1 modified from one prepared by Merz and Ross[10] provides a convenient means of making up mixed fertilizers of definite formulas from various raw materials each of which contains a single plant food constituent.

TABLE 1. WEIGHTS OF SINGLE FERTILIZER CONSTITUENTS REQUIRED (PER TON OF PRODUCT) FOR FERTILIZER FORMULAS

Per cent in Material	Per Cent Desired in Product																				
	½	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
1	1000	2000																			
2	500	1000	2000																		
3	333	667	1333	2000																	
4	250	500	1000	1500	2000																
5	200	400	800	1200	1600	2000															
6	167	333	667	1000	1333	1667	2000														
7	143	286	571	857	1143	1429	1714	2000													
8	125	250	500	750	1000	1250	1500	1750	2000												
9	111	222	444	667	889	1111	1333	1556	1778	2000											
10	100	200	400	600	800	1000	1200	1400	1600	1800	2000										
11	91	182	364	545	727	909	1091	1273	1455	1636	1818	2000									
12	83	167	333	500	667	833	1000	1167	1333	1500	1667	1833	2000								
13	77	154	308	462	615	769	923	1077	1231	1385	1538	1692	1846	2000							
14	71	143	286	429	571	714	857	1000	1143	1286	1429	1571	1714	1856	2000						
15	67	133	267	400	533	667	800	933	1067	1200	1333	1467	1600	1733	1867	2000					
16	62	125	250	375	500	625	750	875	1000	1125	1250	1375	1500	1625	1750	1875	2000				
17	59	118	235	353	471	588	706	824	941	1059	1176	1294	1412	1529	1647	1765	1882	2000			
18	55	111	222	333	444	556	667	778	889	1000	1111	1222	1333	1444	1556	1667	1778	1889	2000		
19	52	105	211	316	421	526	632	737	842	947	1053	1158	1263	1368	1474	1579	1684	1789	1895	2000	
20	50	100	200	300	400	500	600	700	800	900	1000	1100	1200	1300	1400	1500	1600	1700	1800	1900	2000
21	47	95	190	286	381	476	571	667	762	857	952	1048	1143	1238	1333	1429	1524	1619	1714	1810	1905
22	45	91	182	273	364	455	545	636	727	818	909	1000	1091	1182	1273	1364	1455	1545	1636	1727	1818
23	43	87	174	261	348	435	521	608	695	782	869	956	1043	1130	1217	1304	1391	1478	1564	1651	1738
24	41	83	167	250	333	417	500	583	667	750	833	917	1000	1083	1167	1250	1333	1417	1500	1583	1667
25	40	80	160	240	320	400	480	560	640	720	800	880	960	1040	1120	1200	1280	1360	1440	1520	1600
26	38	77	154	231	308	385	462	538	615	692	769	846	923	1000	1077	1154	1231	1308	1385	1462	1538
27	37	74	148	222	296	370	444	519	593	667	741	815	889	963	1037	1111	1185	1259	1333	1407	1481
28	35	71	143	214	286	357	429	500	571	643	714	786	857	929	1000	1071	1143	1214	1286	1357	1429
30	33	67	133	200	267	333	400	467	533	600	667	733	800	867	933	1000	1067	1133	1200	1267	1333
35	29	57	114	171	229	286	343	400	457	514	571	629	686	743	800	857	914	971	1029	1086	1143
40	25	50	100	150	200	250	300	350	400	450	500	550	600	650	700	750	800	850	900	950	1000
45	22	44	89	133	178	222	267	311	356	400	444	489	533	578	622	667	711	756	800	844	889
47	21	43	85	128	170	213	255	298	340	383	426	468	511	553	596	638	681	723	766	809	851
48	21	42	83	125	167	208	250	292	333	375	417	458	500	542	583	625	667	708	750	792	833
49	20	41	82	122	163	204	245	286	327	367	408	449	490	531	571	612	653	694	735	776	816
50	20	40	80	120	160	200	240	280	320	360	400	440	480	520	560	600	640	680	720	760	800
52	19	39	77	116	154	192	231	269	308	346	385	423	462	500	539	577	616	654	693	731	769
54	18	37	74	111	148	185	222	260	297	334	372	406	445	482	519	556	593	625	667	704	741
56	17	36	72	107	143	179	215	250	286	322	357	393	427	465	500	536	577	607	643	679	715
60	16	33	67	100	134	167	200	234	267	300	334	367	400	434	467	500	534	567	600	634	667

In the left-hand column of Table 1 are given the percentages of plant food (from 1 to 60 per cent) in fertilizer materials that may be used in making up complete products; in the 21 columns numbered from ½ to 20, are shown the quantities of these materials required (per ton of product) to give the desired percentage of plant food designated at the head of each column.

To find the amount of material (containing any particular percentage of fertilizer constituent shown in the first column of figures), use the number of pounds of this material shown where the horizontal and vertical lines from the two percentages cross. For instance, if it is desired to produce a mixed fertilizer containing 10 per cent P_2O_5 from 20 per cent superphosphate, pick out figure 20 in the left-hand column and follow along the horizontal line until it crosses the vertical column with the heading 10. The figure at this intersection is 1,000 or the number of pounds of superphosphate required per ton of the desired product.

This same table is applicable to the preparation of definite formulas from fertilizer materials containing two or more plant-food constituents, provided of course that the formulas are not of such a high analysis as to be beyond the capacity of the raw materials to produce.

Triangular System of Computation

Merz and Ross[10] describe a method involving the use of triangular diagrams whereby it can be acertained whether or not a mixed fertilizer of a definite formula can be made from combinations of materials containing more than one fertilizer constituent. They applied this method to the computation of fertilizer mixtures made up from such compounds as potassium nitrate, potassium phosphate and monoammonium phosphate with and without the addition of lower grade materials.

Since this is a convenient and useful method of determining the possibilities and limitations of various organic and inorganic substances in making up mixed products it is of interest to those who manufacture high analysis fertilizers and hence a description of the system and how it is applied is given below:

"Variations in the composition of mixed fertilizers may be represented by use of a system of three coordinates corresponding to the three variables, ammonia, phosphoric acid and potash. Such a system of coordinates is the triangular system, and the range of fertilizer ratios which can be made from fertilizer materials can be readily determined with the aid of triangular section paper as represented in Figure 4.

"The corners A, B, and C of the triangle represent 100 per cent of NH_3, P_2O_5, and K_2O, respectively. The distance from each corner of the triangle to the opposite side is divided into 100 equal parts. The sum of the distances along the respective perpendiculars, from any point within the triangle to the opposite sides, will always amount to 100 of these divisions. Each point within the triangle will therefore represent a definite mixture of all three constituents in such proportion as to total 100 per cent. Thus the point E, being 25, 50, and 25 divisions from the sides BC, CA and AB respectively, represents a mixture in which 25 per cent of the total fer-

tilizing material is NH_3, 50 per cent is P_2O_5, and 25 per cent is K_2O. This point, therefore, represents a 25–50–25 fertilizer ratio, or any submultiple of this ratio, such as 4–8–4. Each side of the triangle represents varying mixtures of the two constituents represented by the adjacent corners, but none of that of the opposite corner. Thus the side AB represents mixtures containing varying amounts of NH_3 and P_2O_5 but no K_2O; and the side CA varying amounts of K_2O and NH_3 but no P_2O_5. Any particular point on a side represents a definite mixture of two constituents. The point D on
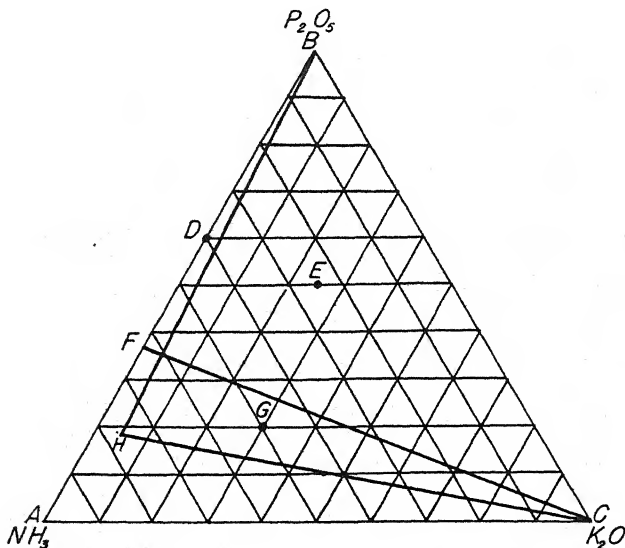
FIGURE 4. Triangular diagram illustrating graphical representation of fertilizer ratios.

the side AB, for example, being 40 divisions from BC and 60 divisions from AC, corresponds to a fertilizer mixture, which contains 40 per cent of the total fertilizing elements as NH_3, 60 per cent as P_2O_5, and 0 per cent K_2O. . .

"A material such as sodium nitrate, in which the NH_3 amounts to 100 per cent of the fertilizing elements present, will be represented on the triangle by the point A. Similarly, superphosphate will correspond to the point B, and a potash salt to the point C. As the lines joining these three points coincide with the boundary lines of the triangle, it follows that submultiples of any fertilizer ratio whatever may be made by combinations of these three materials. The maximum fertilizer analysis formula possible for any given ratio is obtained by multiplying by the factor $\dfrac{2000}{X + Y + Z}$.

Thus, if the sodium nitrate contains 18 per cent NH_3, the superphosphate 16 per cent P_2O_5, and the potash salt 20 per cent K_2O; then, for a 4–8–4 mixture, $X = 444$, $Y = 1000$, $Z = 400$, and $X + Y + Z = 1844$. The maximum possible analysis formula, corresponding to the mixture 4–8–4, that can be made from these materials is therefore $\left[\dfrac{2000}{1844} (4-8-4)^4 \right]$ or 4.34–8.68–4.34.

"A material, for example a tankage containing, say, 8.5 per cent NH_3 and 5 per cent P_2O_5, would have 63 per cent of its fertilizing elements in the form of NH_3 and 37 per cent as P_2O_5, and would be represented in the triangle on the side AB by the point F. Submultiples of all ratios which fall within the triangle FCB can therefore be made from this material in combination with superphosphate and a potash salt, while those which fall outside this triangle, such as the analysis formula 5–2–3 corresponding to the ratio 50–20–30 represented by the point G, cannot be made. G, however, falls within the triangle FCA, and, therefore, submultiples of the ratio 50–20–30 can be obtained by combinations of tankage and potash salt with a nitrogenous material.

"If one-half of the ammonia in a 4–8–4 fertilizer mixture is to be obtained from nitrate of soda, one-fourth from cottonseed meal, and one-fourth from tankage, then 2 of a total of 4 parts of NH_3 will be present in the mixture as nitrate, 1 as cottonseed meal, and 1 as tankage. But the quantities of the two last materials, which contain 1 part each of NH_3, also contain 0.96 part of P_2O_5 and 0.23 part of K_2O. The mixture of these three materials therefore contains 77 per cent of the fertilizer constituents as NH_3, 19 per cent as P_2O_5, and 4 per cent as K_2O and may be represented in Figure 4 by the point H. Submultiples of all ratios, which fall within the triangle HBC can be made by combinations of these three materials with superphosphate and a potash salt. The maximum fertilizer analysis formula that can be made of any of these ratios is obtained in the usual way, by multiplying by the fraction $\dfrac{2000}{X + X' + X'' + Y + Z}$."

The concentrated materials monoammonium phosphate, monopotassium phosphate and potassium nitrate contain combinations of all three fertilizer constituents in groups of two, and all have chemical and physical properties which make them admirably suited for use in fertilizers. Potassium nitrate, obtained from Chilean nitrate and other sources, has long been used to a limited extent in fertilizers. It may also be prepared by treating potassium chloride with nitric acid, such as that produced in the fixation of nitrogen. Monoammonium phosphate is now being used in high-grade fertilizers and may be prepared by neutralizing ammonia, such as obtained in the fixation of nitrogen, with phosphoric acid. The use of

monopotassium phosphate in fertilizers has been limited to experimental tests only. It may be prepared from potassium chloride and phosphoric acid. The percentage composition of these salts is given in Table 2.

TABLE 2. PERCENTAGE COMPOSITION OF SEVERAL CONCENTRATES SUITABLE FOR THE MANUFACTURE OF HIGH ANALYSIS COMPLETE FERTILIZERS

| Salt | Composition on Basis of: | | | | | |
| | Total material | | | Fertilizing elements present | | |
	NH_3 (%)	P_2O_5 (%)	K_2O (%)	NH_3 (%)	P_2O_5 (%)	K_2O (%)
Monoammonium phosphate ($NH_4H_2PO_4$)	14.80	61.72		19.34	80.66	
Monopotassium phosphate (KH_2PO_4)		52.18	34.59		60.14	39.86
Potassium nitrate (KNO_3)	16.85		46.58	26.57		73.43
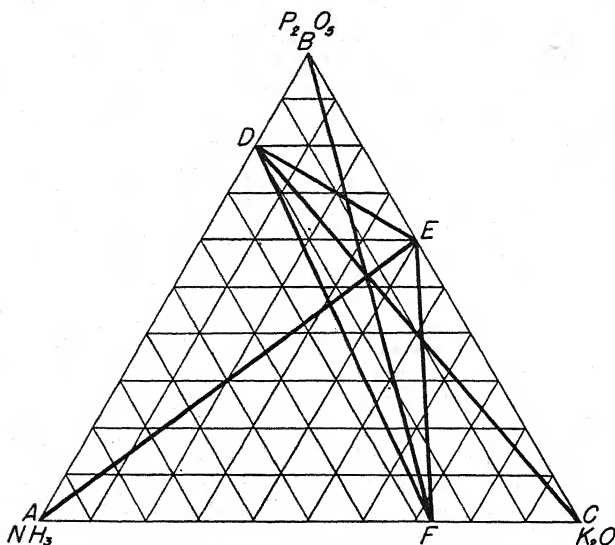
FIGURE 5. Triangular diagram showing fertilizer ratios obtainable from combinations of monoammonium phosphate, monopotassium phosphate, and potassium nitrate, as well as those obtainable from combinations of these compounds with single fertilizer constituent materials.

Applying the triangular system to fertilizer mixtures from concentrated materials it is seen from the percentage values given in Table 2 that monoammonium phosphate corresponds to point D in the triangle of Figure 5;

monopotassium phosphate to point E and potassium nitrate to point F. These three materials may therefore be used to make submultiples of all fertilizer ratios falling within the triangle DEF. In the same way, triangles may be drawn corresponding to combinations of any two of these compounds with a nitrogen, phosphoric acid, or potash salt. Thus the triangle ADE encloses all possible ratios that can be made with mixtures of monoammonium phosphate, monopotassium phosphate, and a nitrogen compound; the triangle CDE all ratios that can be prepared from the same two compounds and a potash salt, and the triangle BDE all the ratios that can be made from these two compounds and a phosphatic material, such as superphosphate.

When each of three materials selected for a mixture contains two fertilizing elements, then the amount of each required to give a ton of a fertilizer of any analysis formula which they are capable of making, as shown by the triangle method, may be calculated as follows: If A, B and C are the percentages respectively of the NH_3, P_2O_5, and K_2O desired in the mixed fertilizer, and

X = Weight of material containing a per cent NH_3, and b per cent P_2O_5
Y = Weight of material containing b' per cent P_2O_5, and c per cent K_2O
Z = Weight of material containing c' per cent K_2O, and a' per cent NH_3

$$\text{Then } X = \frac{2000b'c'A + a'cB - a'b'C}{ab'c' + a'bc}. \tag{1}$$

$$Y = \frac{2000B - bX}{b'}, \quad \text{and} \tag{2}$$

$$Z = \frac{2000C - cY}{c'} \tag{3}$$

For the particular case where the three materials used are monoammonium phosphate, monopotassium phosphate, and potassium nitrate respectively,

$$X, \text{ monammonium phosphate} = 2000 \frac{2430.54A + 582.84B - 879.23C}{71945}$$

$$Y, \text{ monopotassium phosphate} = \frac{2000 - 61.72X}{52.18}$$

$$Z, \text{ potassium nitrate} = \frac{2000C - 34.6Y}{46.58}$$

The number of fertilizer ratios it is possible to make from these materials is limited, as already explained, and the same is true of any three materials which contain two constituents each. However, by successively combining these materials in pairs with ammonia, phosphoric acid and potash salts,

nine possible combinations are obtained which can be used by varying the materials in any combination to make any fertilizer ratio whatever. In Table 3 are given expressions for calculating each of these nine combinations, the quantities of the materials required for any fertilizer formula falling within the triangle, representing the combination in Figure 5.

For further details concerning the computation of fertilizer mixtures, conforming to the 52 analyses adopted by conferences of agronomists and fertilizer manufacturers as standard for 24 states, the reader is referred to the original article of Merz and Ross[10].

Fertilizer Conditioners

As indicated in the early part of this chapter, virtually all of the complete fertilizers offered to the consummer contain certain quantities of relatively inert materials. While these do not add any plant-food constituent to the finished product, they do not adversely affect the value of the final product. These so-called fillers serve a dual purpose: (1) they make it feasible to produce fertilizers having definite formulas; (2) they improve the physical condition of the final product by reducing hygrosopicity, minimizing its tendency to cake and set and thus facilitate the handling of the fertilizer in the factory and its distribution in the field.

Before the bulky organic by-products such as cottonseed meal and animal and garbage tankage were diverted to other uses, the conditioning of mixed fertilizers was not a major problem since the free-flowing properties of these fillers were not greatly affected by the presence of substantial percentages of free moisture. Moreover, the low-analysis fertilizers of several decades ago made it possible to condition goods with large quantities of these organics, as well as mineral fillers (chiefly silica sand).

The advent of higher analysis fertilizers made up with fairly pure salts, triple superphosphate and certain other manufactured concentrates, not only greatly reduced the amount of filler required, but imposed the additional problem of obtaining suitable materials in small bulk that would impart the desired physical condition to these products.

The ammoniation of superphosphate and mixed goods (discussed in Chapter 17), did much toward improving the mechanical condition of concentrated fertilizers by altering the chemical and physical nature of the constituents before they were stored and shipped, but it was also necessary to study the effect of various solid additives with a view to determining those which could be incorporated in high-analysis products to improve their mechanical properties without adversely affecting their fertilizer value. One of the most satisfactory of these additives which appears to meet these requirements under normal conditions is dolomite or dolomitic limestone.

TABLE 3. EXPRESSIONS FOR CALCULATING THE QUANTITIES OF MATERIAL REQUIRED FOR A TON OF AN A–B–C FERTILIZER WHEN MATERIALS THAT CONTAIN TWO FERTILIZING ELEMENTS ARE COMBINED IN PAIRS WITH AN NH_3, P_2O_5, OR K_2O SALT

Mixture of—	X	Y	Z	M_{NH_3}	M_{K_2O}	$M_{P_2O_5}$
$X + Y + M_{K_2O}$	$\dfrac{2{,}000A}{a}$	$\dfrac{2{,}000B-bX}{b}$			$\dfrac{2{,}000C-cY}{c''}$	
$X + Y + M_{NH_3}$	$\dfrac{2{,}000B-b'Y}{b}$	$\dfrac{2{,}000C}{c}$		$\dfrac{2{,}000A-aX}{a''}$		
$X + Y + M_{P_2O_5}$	$\dfrac{2{,}000A}{a}$	$\dfrac{2{,}000C}{c}$				$\dfrac{2{,}000B-bX-b'Y}{b''}$
$Y + Z + M_{NH_3}$		$\dfrac{2{,}000B}{b'}$	$\dfrac{2{,}000C-cY}{c'}$	$\dfrac{2{,}000A-a'Z}{a''}$		
$Y + Z + M_{P_2O_5}$		$\dfrac{2{,}000C-c'Z}{c}$	$\dfrac{2{,}000A}{a'}$			$\dfrac{2{,}000B-b'Y}{b''}$
$Y + Z + M_{K_2O}$		$\dfrac{2{,}000B}{b'}$	$\dfrac{2{,}000A}{a'}$		$\dfrac{2{,}000C-cY-c'Z}{c''}$	
$Z + X + M_{K_2O}$	$\dfrac{2{,}000B}{b}$		$\dfrac{2{,}000A-aX}{a'}$		$\dfrac{2{,}000C-c'Z}{c''}$	
$Z + X + M_{NH_3}$	$\dfrac{2{,}000B}{b}$		$\dfrac{2{,}000C}{c'}$	$\dfrac{2{,}000A-a'Z-aX}{a''}$		
$Z + X + M_{P_2O_5}$	$\dfrac{2{,}000A-a'Z}{a}$		$\dfrac{2{,}000C}{c'}$			$\dfrac{2\,000B-bX}{b''}$

X, quantity of material containing a per cent NH_3 and b per cent P_2O_5.
Y, quantity of material containing b' per cent P_2O_5 and c per cent K_2O.
Z, quantity of material containing c' per cent K_2O and a' per cent NH_3.
M_{NH_3}, quantity of material containing a'' per cent NH_3.
$M_{P_2O_5}$, quantity of material containing b'' per cent P_2O_5.
M_{K_2O}, quantity of material containing c'' per cent K_2O.

MacIntire and his co-workers[8, 9] showed that although ordinary lime-stone decreased the solubility of the P_2O_5 in stored superphosphate at ordinary temperatures, dolomite caused no appreciable reduction in the availability of this fertilizer ingredient.

Beeson and Ross[1] found that while dolomite reacts with monoammonium phosphate in the presence of moisture to form phosphates of calcium, magnesium and ammonia, no loss of ammonia or decrease in the availability of the P_2O_5 occurs at ordinary temperatures regardless of the proportions of the reacting materials. These investigators represented the reactions involved at ordinary temperatures (30°C) as follows:

$$3NH_4H_2PO_4 + CaCO_3 \cdot MgCO_3 \rightarrow MgNH_4PO_4 + (NH_4)_2HPO_4 + 2H_2O + 2CO_2$$
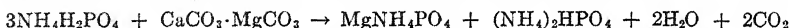
At relatively high temperatures (90°C), however, a more basic phosphate of lime is formed of reduced solubility. Kennen and Morgan[7] reached a similar conclusion when investigating the composition of stored mixed fertilizers containing dolomite.

Although concentrated fertilizer formulas may be prepared using ordinary silica sand as a filler, dolomite has the advantage of neutralizing excess or potential acidity[11], further improving physical condition and furnishing an appreciable quantity of available magnesia which is recognized as a distinct advantage on certain soils and crops.

The Mechanical Mixing of Fertilizers

The final step in the preparation of complete fertilizers is based largely on the blending of several different types of solid materials (including the filler or conditioner). The mixing of solids with solids to obtain a final product from which samples can be drawn of identical composition is virtually impossible, unless the individual constituents are reduced to an impalpable powder. This is not economically feasible in the case of a relatively low-priced product such as fertilizer, but blends can be obtained which will meet the specifications, provided care is exercised in the preparation of the individual materials entering into the complete products. Moreover, the development of ammoniacal solutions that permeate, partially dissolve and react with some of the constituents in the fertilizer materials have contributed greatly to the uniformity of complete products.

It is obvious that the materials must be milled and screened before going to the mixer and though the difference in the friability of these materials is such that milling under the same conditions does not produce the same proportion of the various sizes in each case, subsequent screening insures that the maximum size particles in all materials are approximately identical.

The equipment employed in blending solid fertilizer materials usually consists of a steel cylinder rotating on a horizontal axis. The inner walls of

this cylinder are fitted with flights (bolted to the shell) the object of which is to lift the solid mixture, carry it upward and shower it back onto the material in the bottom of the machine as the cylinder revolves. Thus a circulation is obtained which causes the intermingling of the various fertilizer constituents and as uniform a mixture as the mechanical conditions will permit. The flights are not usually parallel to the axis of rotation but are so arranged that they move the material back and forth so that uniform mixing is obtained in all parts of the cylinder.

Whereas, nearly all drum-mixers operate on the same general principle, they vary with respect to the ratio of diameter to length. One has a rather short axis length and contains a funnel-like chute into which the solids carried up by the flights are discharged. This chute in turn, re-introduces the material into the bottom of the cylinder where the cycle is repeated. This type of mixer receives its materials and empties the complete mixture through the same end of the drum. Since there is only one rotating seal to maintain in this type of mixer, it may be used as an ammoniator by insertion of a spray pipe.

Other types of fertilizer mixers are designed like the equipment used in mixing cement, with a feed at one end and a swinging spout for discharging at the opposite end. Still another type receives its charge at one end and empties the product in the center of the cylinder through sliding ports activated by a cam mechanism.

Practically all cylindrical mixers of the drum type are mounted on trunions and driven through a ring gear. It is needless to say that the periphery speed of the cylinder must be kept below that at which centrifugal force tends to hold the solid ingredients against the walls and prevents the proper discharge of the material carried up by the flights. The speed recommended is usually from 50 to 75 per cent of that at which centrifugal force overcomes the force of gravity.

A rather radical departure from the rotating drum type is one consisting of a stationary vertical steel shell fitted with series of funnels and upwardly pointed cones. As the materials are introduced at the top of the cylinder the various shaped baffles cause them to persue an interrupted and tortuous path as they work their way to the bottom of the chamber, resulting it is claimed, in a thorough mixing of the various ingredients. This type of mixer has no moving parts other than the control values.

All materials delivered to the mixer must be weighed before blending and this may be done in a variety of ways. The type of proportioning equipment is selected according to its applicability to the conditions of each particular fertilizer plant. The most modern method is one in which weighed charges are made up by use of interlocking electrical devices.

Since certain of the raw materials used in concentrated complete fer-

tilizers tend to cake and hence are difficult to mix uniformly, provisions must be made to take care of such conditions. Materials of this type may be carried by a bucket elevator to a hopper which serves as a feed bin for the drum mixer. A coarse screen at the foot of the elevator serves to keep out large lumps of caked material which are crushed to a size permitting them to pass the screen. A further reduction in size is made at the top of the elevator where the material is discharged on a small mesh vibrating screen. The undersize then passes to the drum feed bin and the oversize goes to a hammermill or disintergrator (of the cage type) for further grinding. It 'is then again discharged into the bucket elevator and rescreened before going to the mixer.

After the blended materials are discharged from the mixing drum they are conveyed to storage bins or direct to bagging machines where definite weights are packaged for shipment. Bagging technique varies all the way from hand-filling, hand-weighing and hand-sewing of burlap or other types of cloth bags for export, to the automatic filling, weighing and closure of valved paper bags. In the latter type the placing of the empty bags on the filling nozzle and tipping off the filled packages onto a conveying belt or truck which carries them to storage or direct to the loading platform are the only manual operations required.

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23. Phosphate Leavening Agents

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HISTORICAL

Large quantities of highly purified phosphate compounds are annually consumed in the form of phosphate-containing baking powders and leavening agents. The leavening or aeration of bread doughs for the purpose of making light, sponge-like baked products has been practiced for many centuries. The Egyptians are said to have practiced the art of leavening and to have passed the knowledge along to the Greeks, who later passed it on to the Romans[3].

The early leavening practice involved the growing of yeast cells in dough and batter mixtures. The enzymes of the yeast acted on the flour carbohydrates of the dough and produced carbon dioxide gas and alcohol. The carbon dioxide thus generated was partially trapped within the dough, causing it to expand (or rise). The expanded dough when heated sufficiently became solidified, forming a porous sponge-like bread product.

Yeast leavening today is practiced in much the same manner except for the many refinements in the quality of the yeast and formulation of dough mixtures. Yeast was substantially the only leavening means employed until well into the nineteenth century, when chemical leavening agents began to make their appearance. U. S. Patent No. 2816 of 1842 (Abel Conant) discloses the mixing of tartaric acid, cream of tartar, alum, or other dry acids with flour and subsequently using the flour with an aqueous solution of soda to prepare doughs for baking.

Whereas yeast continues to play an important role in the baking industry, the use of chemical leavening agents has expanded to the point where the manufacture of such agents represents an important sector of the chemical manufacturing industry of this country.

Chemical leavening is accomplished by generation of a leavening gas in the dough either through thermal decomposition of certain gas-producing compounds or by causing a chemical reaction to take place in the dough mixture between an acidic component and a carbonate salt. In either case carbon dioxide gas is liberated causing the dough to puff up or rise before or in the early stages of the baking operation.

Chemical leavening offers a number of advantages over yeast leavening

in the making of many baked products such as biscuits, cakes, waffles, pancakes, etc. Some of these advantages are as follows:

(1) It avoids the long period of time required for the generation of leavening gas in yeast doughs.

(2) It permits uniformity in leavening capacity.

(3) It enables the baker to predetermine the desired amount of leavening gas needed for specific types of baked goods.

(4) The stability and keeping qualities of the chemical agents permit their storage without special precautions other than keeping them dry.

Other advantages and disadvantages might be enumerated but the above are sufficient to show why chemical leavening is so widely practiced at the present time.

Theoretically a large number of carbonate salts might be used as sources of carbon dioxide in chemical leavening, but it has been found most convenient and desirable for a number of reasons to select sodium bicarbonate ($NaHCO_3$) (baking soda) as the substantially universal source of carbon dioxide leavening gas.

Sodium bicarbonate has been used alone as a leavening agent and still is employed to some extent, the leavening action being due to thermal decomposition resulting from the heat of the oven. The decomposition products are carbon dioxide gas and residual normal sodium carbonate (Na_2CO_3). The high alkalinity of the residual salt often produces a yellowish color and undesirable taste in the baked product. However, Davis and Maveety[7] have shown that 1.5 pounds per barrel (196 lbs) of flour may be used without imparting an unpleasant taste to the baked product.

Progress made in the development of chemical leavening agents has been largely confined to the search for suitable acidic compounds which will react with sodium bicarbonate in dough mixtures to liberate carbon dioxide gas at a desirable rate and yet not introduce objectionable and unpalatable residues in the baked products. Some of the acids which have been been proposed for this purpose are tartaric acid, acid tartrates, lactic acid[28], monosodium phosphate, monocalcium phosphate, sodium acid pyrophosphate, phthalic anhydride[29], gluconic acid[30], mellitic acid[31], calcium acid lactate[32], calcium acid pyrophosphate, sodium aluminum sulfate, etc. Of these the tartrates, monocalcium phosphates, sodium aluminum sulfate and sodium acid pyrophosphate have been extensively employed in the baking industry.

According to L. H. Bailey[3] the first baking powder formula used in the United States was developed in 1850. A cream of tartar baking powder was placed on the market in that year. In 1853 V. C. Price produced a baking powder composition comprising cream of tartar, sodium bicar-

bonate, and starch or flour. Tartrate-type baking powders have been on the market since that time and are still used.

Early Phosphate Leavening Agents

Phosphate baking acids were first introduced by E. N. Horsford in 1856 as substitutes for cream of tartar. In that year Horsford obtained U. S. Patent No. 14722 for the preparation of a monocalcium phosphate baking acid from charred bones. The product was marketed as "Horsford's Bread Preparation"[17] in a paper package provided with separate containers for the sodium bicarbonate and the starch-filled monocalcium phosphate product. The housewife was instructed to use two parts of the acid preparation to one part of soda. Horsford was quite active in improving and promoting phosphate baking preparations. This is evidenced by the number of patents on the subject issued in his name between 1856 and 1880.[12] Complete phosphate baking powder mixes were difficult to preserve because absorption of moisture from the air caused them to deteriorate; consequently the early baking powders were sold in glass bottles. It was not until 1893 that such powders were made with sufficient stability to enable them to be packed and marketed commercially in tin cans[3]. According to Bailey[3] a significant improvement in the manufacture of monocalcium phosphate was introduced in 1889 whereby the neutralizing strength was raised from 45 to 50 per cent to approximately 80 per cent. The improvement consisted in neutralizing the excess acidity of the monocalcium phosphate paste with finely milled bone ash instead of drying the paste with starch.

Ammonium and potash alums were introduced as cream of tartar substitutes rather soon after the latter material came into general use as a chemical leavening acid, but it was not until about 1892[3] that the use of sodium aluminum sulfate as a leavening acid became established.

Because of its relatively low price sodium aluminum sulfate soon gained a substantial foothold in the baking powder field. In spite of much detrimental publicity[20] against the use of aluminum compounds in food products sodium aluminum sulfate has continued to enjoy success in the field, and today it is used quite extensively in combination baking powders where it is admixed with monocalcium phosphate. Much of the baking powder used in the home is of this type. Substantially no straight sodium aluminum sulfate-type powders are now being used.

Modern Phosphate Baking Acids

The principal phosphate baking acids on the market today are monocalcium phosphate monohydrate, anhydrous monocalcium phosphate and sodium acid pyrophosphate. Other phosphate baking acids such as mono-

sodium phosphate, calcium acid pyrophosphate, sodium aluminum phosphate, etc., have been proposed or used to some extent but are not of sufficient importance to warrant detailed consideration at this time. Monosodium phosphate was employed for several years in a baking powder composition but its use has been discontinued because of its instability in moist atmospheres. Calcium acid pyrophosphate was proposed as a baking acid by W. B. Brown and R. A. Holbrook[5] in 1911. More recently R. J. Hurka[13] has proposed to use calcium acid pyrophosphate containing a minor proportion of alkali metal metaphosphate. Others have investigated the possibilities of calcium acid pyroposphate but so far no appreciable use of the compound has resulted.

Monocalcium phosphates are more extensively used than all other chemical leavening acids. It is estimated that more than 78,000,000 pounds[27] of such phosphates are consumed annually in the United States. Monocalcium phosphate is available in powdered form where all of the particles will pass through a 140-mesh screen, with 65 to 85 per cent through 200 mesh. It is also available in granular form where the particles pass an 80-mesh screen and are retained on a 200-mesh screen. The different types of product include the crystalline monohydrate in the form of solid crystalline, agglomerated, or spray-dried spherical particles, and the anhydrous salt in the form of heat treated (or coated) solid particles. Each of these products has certain chemical or physical characteristics which offer advantages in specific baking applications. For example, the powdered monohydrated phosphates and the coated anhydrous salt are especially suitable for use in self-rising and phosphate flours, whereas the granular products are used extensively in straight phosphate baking powders. Both the powdered and granular materials are adaptable for use in combination powders. The coated anhydrous salt is particularly suitable for biscuits and the like where a slow reaction rate in the dough mixing stage is important.

Sodium acid pyrophosphate is also produced on a large scale, principally in the form of a fine powder. It is extensively used in making doughnuts, cakes and packaged biscuit doughs.

The monocalcium phosphate and sodium acid pyrophosphate baking acids on the market today are substantially pure chemical compounds except where the compositions have been formulated to include controlled amounts of certain components in order to yield products having definite characteristics. For example, small amounts of potassium, aluminum, etc., are beneficial in the production of coated anhydrous monocalcium phosphate. Some dicalcium phosphate is present in all monocalcium phosphates. This is formed as a result of the lime used to eliminate free acidity in the products. All of the compositions are substantially free of elements such as lead, arsenic, and fluorine, meeting all government requirements with respect to such elements.

Neutralizing Strength

The measure of the capacity of a baking acid to react with sodium bicarbonate is termed its neutralizing strength. This is expressed as parts by weight of the acid salt required to neutralize exactly 100 parts of sodium bicarbonate. Following are the generally accepted equations representing the final reactions which take place between sodium bicarbonate and three of the acid phosphate salts employed in baking powders and salt-rising flours:

$$3CaH_4(PO_4)_2H_2O + 8NaHCO_3 \rightarrow 8CO_2 + Ca_3(PO_4)_2 + 4Na_2HPO_4 + 11H_2O$$

| *Monocalcium Phosphate* | *Sodium Bicarbonate* | *Carbon Dioxide* | *Tricalcium Phosphate* | *Disodium Phosphate* | *Water* | (1) |

$$NaH_2PO_4H_2O + NaHCO_3 \rightarrow CO_2 + Na_2HPO_4 + 2H_2O$$

| *Monosodium Phosphate* | *Sodium Bicarbonate* | *Carbon Dioxide* | *Disodium Phosphate* | *Water* | (2) |

$$Na_2H_2P_2O_7 + 2NaHCO_3 \rightarrow 2CO_2 + 2Na_2HPO_4 + H_2O$$

| *Sodium Acid Pyrophosphate* | *Sodium Bicarbonate* | *Carbon Dioxide* | *Disodium Phosphate* | *Water* | (3) |

According to the above equations, the theoretical neutralizing strength of monocalcium phosphate, monosodium phosphate and sodium acid pyrophosphate in terms of 100 parts of sodium bicarbonate are 88.9, 74.3 and 60.9 respectively.

Although baking acids are valued largely on the basis of their capacity to react with sodium bicarbonate, the theoretical neutralizing strength is seldom if ever attained with commercial phosphates unless free phosphoric acid is present. This free acid adversely affects the physical or mechanical condition of the product, causing the baking powder manufactured therefrom to have poor keeping qualities and upsets its even action in the mixing and baking processes. Therefore, though the neutralizing strength of pure monocalcium phosphate (according to equation (1) is 88.89, it is seldom desirable to manufacture a product with a neutralizing strength above 86. Such a product contains as a rule enough dicalcium phosphate to insure the absence of free phosphoric acid with its attendant difficulties in drying and mixing and its probable premature reaction when mixed with sodium bicarbonate.

In the preparation of baking powder from monocalcium phosphate or any other baking acid it is also most important that little or no excess of sodium bicarbonate is present over that which will be acted upon by the acid salt, since the heat of the oven will decompose this excess producing normal sodium carbonate which, as previously stated, tends to give a yellow color and unpleasant taste to the baked product.

The neutralizing strength may be determined by titrating the baking acid with a standard alkali solution, or by reacting the acid with sodium bicarbonate and measuring the amount of CO_2 gas evolved. Neither of these methods gives results which can be relied upon in all cases to accurately indicate the neutralizing strength obtainable in actual baking operations. Adler and Barber[1] proposed to modify the titration method whereby an excess of standard alkali is employed, and the excess back titrated with a standard hydrochloric acid solution. They claim to obtain more consistent and accurate indications of the true neutralizing strength by this procedure. This modified method is now generally employed by the trade.

Table 1 gives typical chemical and particle size analyses and calculated compositions of the principal monocalcium phosphate baking acids which have been produced in this country within the past few years.

Table 2 gives the composition of two typical sodium acid pyrophosphate baking acids now being sold in the United States.

Manufacture of Monocalcium Phosphates

Disregarding the earlier manufacture of crude calcium acid phosphate for fertilizer purposes, the first manufactured for food purposes appears to be that described by E. Horsford in U. S. Patent 14,722 (1856). This patent describes the process which comprises reacting partially charred bones with sulfuric acid to form calcium sulfate and phosphoric acid. The calcium sulfate was filtered off and the liquid phosphoric acid concentrated in iron kettles. Bone ash in calculated amounts was added to the acid, forming a pasty calcium acid phosphate compound, which was then mixed with starch or flour. After drying for several weeks the material was ground to form a dry acid phosphate powder, two parts of which were capable of neutralizing one part of sodium bicarbonate.

From this crude beginning many improvements have been made in the quality and physical properties of phosphate baking acids through systematic research and a number of distinct types of high quality monocalcium phosphate are now being produced.

The raw materials required in modern methods for manufacturing monocalcium phosphates are limited to substantially pure hot lime (CaO) or hydrated lime ($Ca(OH)_2$) and highly purified phosphoric acid. Most of the phosphoric acid used is now produced by the burning of pure elemental phosphorus followed by hydration of the resulting phosphoric anhydride. The acid is of such high purity that in many cases it is modified by the addition of certain impurities such as potassium, aluminum, magnesium, etc., in small amounts. These elements affect primarily the physical characteristics of the monocalcium phosphate particles which in turn affect the reaction characteristics of the product.

Batch Type

The regular batch type of monocalcium phosphate is made by placing a weighed amount of phosphoric acid of about 75 per cent strength in a stainless steel or ceramic-lined batch tub equipped with efficient agitators. Hot lime in slightly less than the calculated amount for the equation $CaO + 2H_3PO_4 \rightarrow CaH_4(PO_4)_2 \cdot H_2O$ is added at such rate that the temperature of the batch is maintained at about 75 to 110°C. Near the end of the reaction period the final traces of free phosphoric acid are neutralized with hydrated lime. The resulting product is a fairly dry lumpy material which is further dried under controlled temperature conditions and milled. The milled material is then screened or air separated into granular and powder products and bagged. The above procedure is considered typical, though different manufacturers may vary the detail of operations to a considerable extent. The granular product is principally used in baking powders, whereas the powdered product finds its greatest use in self-rising and phosphated flours. Phosphates produced by processes of this kind are in the form of irregular particles consisting of agglomerations of very fine crystals of monocalcium phosphate monohydrate together with a small amount of dicalcium phosphate and other impurities which were present in the raw materials. Figure 1 shows the general character of the particles comprising this type of product.

Crystalline Type

A crystalline monocalcium phosphate in the form of clear, solid, plate-like monohydrate crystals is shown in Figure 2. According to C. H. Milligran[19] a product of this type may be made by introducing lime and a strong phosphoric acid solution simultaneously and in equivalent amounts into a phosphoric acid of at least 50 per cent concentration while maintaining a temperature of at least 80°C. during the reaction. Crystals of monocalcium phosphate form as the solution becomes saturated. After the crystals have grown to the desired size the mixture is passed through a cooling zone where further crystallization and growth of crystals takes place. The solid crystals are then removed from the strong acid mother liquor by centrifuging or other means, and the mother luquor being returned to the process. The separated crystals are washed substantially free of adhering phosphoric acid and the last traces of such free acid neutralized with a base such as hydrated lime.

Spray-Dried Type

Spray-dried monocalcium phosphate (monohydrate) is made by reacting a lime base with a phosphoric acid solution of sufficient dilution to yield a liquid slurry or solution of monocalcium phosphate, and spraying

TABLE 1. CHEMICAL ANALYSES AND ESTIMATED COMPOSITION OF SEVERAL TYPICAL MONOCALCIUM PHOSPHATE BAKING ACIDS SOLD IN THE UNITED STATES*

Baking acid	A	B	C	D	E	F	G
Type	Crystalline	Regular	Regular	Regular	Spray dried	Coated anhydrous	Granular
Neutralizing value	85.4%	84.4%	81.5%	82.0%	83.2%	85.8%	81.8%
Free acid	None	None	None	None	None	None	None
Acid insoluble	0.15	0.13	0.23	0.09	0.10	0.11	0.13
Moisture	0.06	0.41	0.28	0.60	0.29	None	0.41
Loss on ignition	21.5	20.69	20.50	21.22	20.83	15.35	20.30
Water soluble P_2O_5	52.9	52.3	51.5	50.9	50.7	53.0	50.76
Total P_2O_5	56.0	55.8	55.75	55.6	55.6	59.0	55.6
CaO	23.0	22.62	23.1	23.4	23.6	24.75	23.29
MgO	0.04	0.21	0.14	0.18	0.09	0.18	0.23
Fe and $AlPO_4$	0.10	0.13	0.16	0.30	0.15	0.65	0.15
$FePO_4$	0.03	0.07		0.05	0.07	0.07	0.07
SO_3	0.02	0.23	0.23	0.17	0.24	0.26	0.25
K_2O	0.04	0.22	0.06			0.65	
Na_2O	0.04	0.50	0.40			0.09	
Pb	0.3 ppm	1.2 ppm	1.6 ppm	0.3 ppm	0.3 ppm	1.0 ppm	1.3 ppm
F	5.3 ppm	2.9 ppm	19.0 ppm	10.0 ppm	4.0 ppm	3.6 ppm	3.0 ppm
As_2O_3	0.1 ppm	0.3 ppm	0.3 ppm	0.1 ppm	0.1 ppm	0.3 ppm	0.3 ppm

Sieving:							
On 40 mesh	None				None	None	None
60 mesh	0.1	None		Trace	0.1	None	Trace
80 mesh	0.4	None		0.2	0.5	Trace	Trace
100 mesh	0.5	Trace	0.3	0.4	0.6	Trace	1.2
120 mesh	1.5	0.5	3.3	4.7	7.9	0.1	24.0
140 mesh	24.4	1.5	5.9	4.9	15.6	0.4	39.8
200 mesh	37.2	11.8	17.5	8.9	19.7	2.1	30.0
325 mesh	19.0	26.0	28.0	21.1	25.7	13.0	1.8
Through 325 mesh	16.9	60.2	45.0	59.8	29.9	84.4	3.2
Calculated composition (acidic components):							
$Ca(H_2PO_4)_2 \cdot H_2O$	93.70	91.60	90.50	89.00	89.40	86.60	88.80
$Ca(H_2PO_4)_2$	5.82	6.60	7.95	7.80	9.22	10.80	9.10
$CaHPO_4$	0.23	1.24	0.82	1.05	0.53	0.98	1.36
$Mg(H_2PO_4)_2 \cdot H_2O$							
$Mg(H_2PO_4)_2$							

* Unpublished analytical data supplied by Mr. J. R. Schlaeger (Victor Chemical Works).

such solution into a heated drying atmosphere whereby the excess moisture is removed yielding a product consisting of small, substantially spherical particles.

At least three different manufacturers have taken out patents (U. S. 1442318 Jan. 16, 1923 C. T. Whittier; U. S. 1689697 Oct. 30, 1928 E. W. Thornton; U. S. 1818114 Aug. 11, 1931 J. Carothers and P. Logue) relating to spray-dried monocalcium phosphate and methods of manufacture. Carothers and Logue describe a process whereby milk of lime having a specific

TABLE 2. COMPOSITION OF TWO TYPICAL COMMERCIAL SODIUM ACID PYROPHOSPHATE BAKING ACIDS*

	(1)	(2)
$Na_2H_2P_2O_7$	96.60%	96.20%
NaH_2PO_4	0.80	0.70
Fe and $AlPO_4$	0.015	0.105
$AlPO_4$	Trace	0.10
P_2O_5	63.40	63.90
Acid insoluble	0.01	0.003
SO_2	0.02	0.01
F	3.0 ppm	2.0 ppm
Pb	1.2 ppm	0.8 ppm
As	0.2 ppm	0.1 ppm
pH (1.0% soln.)	4.5	4.11
Neutralizing value	72.6	72.0
Sieving:		
On 100 mesh	0.6%	0.2%
200 mesh	10.9	9.6
325 mesh	19.0	16.9
Through 325 mesh	69.5	73.3

* Unpublished analytical data supplied by Mr. J. R. Schlaeger (Victor Chemical Works).

gravity of approximately 1.1 is added slowly to a 75 per cent phosphoric acid solution, with vigorous agitation, until approximately 5 per cent excess lime has been added to form a slurry of monocalcium phosphate. This slurry is then sprayed into a chamber through which a current of hot air is passed causing the fine slurry droplets to solidify into small dry spherical particles of monocalcium phosphate containing substantially no free acid, but a small amount of dicalcium phosphate. Figure 3 illustrates the physical form of a commercial spray-dried product. One of the outstanding feature of this type product is its free-flowing characteristics.

Anhydrous Monocalcium Phosphate

Anhydrous monocalcium phosphate ($CaH_4P_2O_8$) has long been known but has not found much application in the leavening agent field because
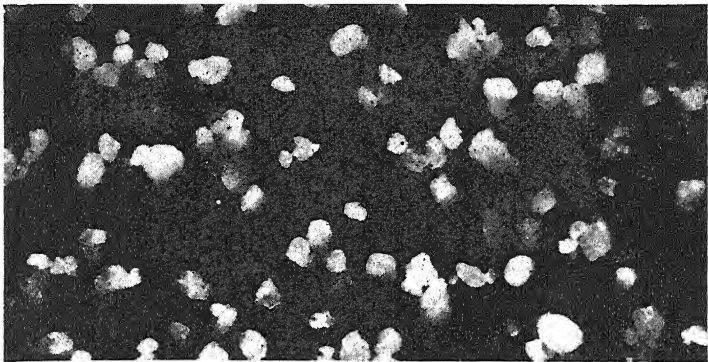
FIGURE 1. Photomicrograph A-Particles of monocalcium phosphate (monohydrate). Magnified to 85 diameters.

FIGURE 2. Photomicrograph B-Crystals of monocalcium phosphate (monohydrate). Magnified to 85 diameters.
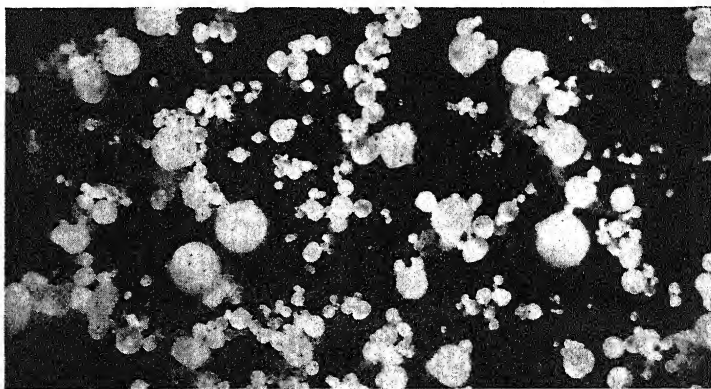
FIGURE 3. Photomicrograph C-Spray-dried monocalcium phosphate (monohydrate). Magnified to 85 diameters.

of its instability against absorption of atmospheric moisture. However, for the past 10 years a specially coated anhydrous monocalcium phosphate[6] has been successfully employed as a baking acid in baking powders, self-rising flours, etc.

This special type of anhydrous monocalcium phosphate, developed by Schlaeger[24] and Knox *et al.*[14], is made by reacting lime with a strong phosphoric acid containing minor amounts of certain metal compounds, such as potassium, aluminum, etc., at a sufficiently high temperature (above 140°C) to prevent the formation of any substantial amount of hydrated monocalcium phosphate, and at a temperature low enough to prevent the formation of any appreciable amount of pyrophosphate. The reaction is carried out in a batch mixer equipped with an efficient agitator. The resulting product in the form of minute crystals of anhydrous monocalcium phosphate is heat-treated at a temperature of approximately 200 to 220°C. Under these conditions the potassium and several other elements appear to combine with the calcium phosphate surface of the crystals to form an autogenous, glass-like, substantially water-insoluble coating over the crystals.

When this new phosphate is used as a baking acid or acid constituent of baking powders the glass-like coating permits only a slow penetration of water into the interior of the particle and thereby delays its reaction with the sodium bicarbonate in the dough mixture.

Figure 4 illustrates the physical form of the heat-treated anhydrous monocalcium phosphate particles. Figure 5 represents the coating shell (magnified to 800 diameters) remaining after the anhydrous monocalcium phosphate has been dissolved from the interior with distilled water. The solid particles clinging to the coating surface are probably dicalcium phosphate particles.

MANUFACTURE OF SODIUM ACID PYROPHOSPHATE

Sodium acid pyrophosphate is generally made by partially dehydrating monosodium acid orthophosphate in accordance with the following equation:

$$2NaH_2PO_4 + heat \rightarrow Na_2H_2P_2O_7 + H_2O$$
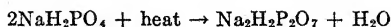
The reaction is usually carried out in a rotary-type converter in a continuous manner. The monosodium phosphate is fed into one end and is heated to a temperature of 225 to 250°C by passing hot gases of combustion through the convertor in direct contact with the material, or by passing the hot gases through a jacket surrounding the converter chamber. By carefully controlling the time and temperature conditions the monosodium phosphate is almost completely converted to sodium acid pyrophosphate
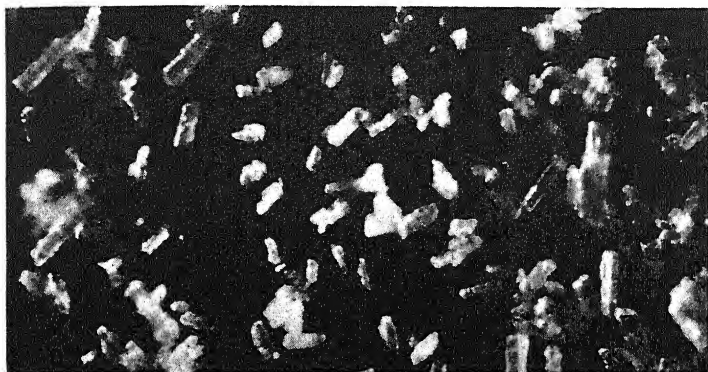
FIGURE 4. Photomicrograph D-Coated crystalline anhydrous monocalcium phosphate. Magnified to 85 diameters.
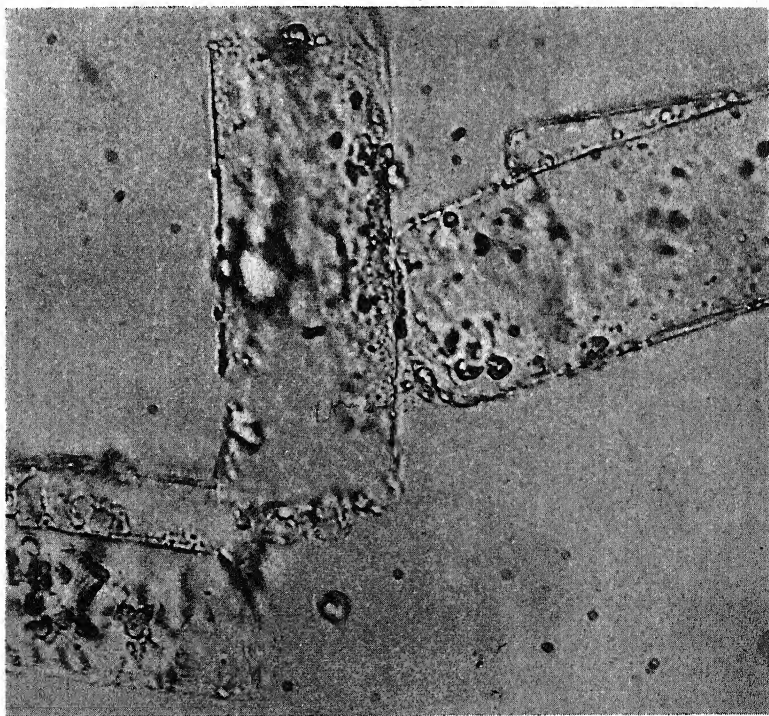
FIGURE 5. Photomicrograph E-Coating shell remaining after solution of anhydrous monocalcium phosphate from interior with distilled water. Magnified to approximately 800 diameters.

when it reaches the discharge end of the converter. The heating period usually extends over a number of hours.

Variations in the baking quality of the sodium acid pyrophosphate product may be effected by varying the type of monosodium orthophosphate starting material, as well as the conversion conditions. The monosodium orthophosphate starting material may be produced in pure crystalline form from a saturated solution, or by a batch process whereby substantially pure phosphoric acid is reacted with soda ash or caustic soda in correct proportions and the whole solidified into a granular mass. Other means of producing the starting material have been suggested such as spray drying[18] a hot concentrated solution of monosodium phosphate, or by rapidly drum-drying the solution[11].

By utilizing the above types of monosodium phosphate and controlling the conversion conditions either fast or slow acting types of sodium acid pyrophosphates may be produced. Hetzel and Taylor[11] claim that sodium acid pyrophosphate may be obtained by rapidly drum-drying a concentrated solution of monosodium phosphate containing small amounts of potash and alumina and heating the product at 225 to 235°C in an atmosphere containing controlled amounts of water vapor.

C. R. McCullough[16] describes a process of converting monosodium phosphate to sodium acid pyrophosphate at relatively high temperatures in a short period of time by controlling the water vapor pressure during conversion to prevent formation of sodium metaphosphate impurities in the product. Sodium metaphosphate has no value as a baking acid.

LEAVENING REACTIONS AND BAKING TESTS

The chemical reactions involved in the phosphate leavening of bakery products are quite complex and there is no unanimity of opinion by the various authorities regarding reactions which actually take place in dough mixtures.

The reaction between monocalcium phosphate and sodium bicarbonate in doughs may proceed according to one or more of the following equations, depending on the relative amounts of the two components reacting and the conditions of time, temperature and dough formulation.

$$3CaH_4(PO_4)_2 + 8NaHCO_3 \rightarrow Ca_3(PO_4)_2 + 4Na_2HPO_4 + 8H_2O + 8CO_2 \quad (1)$$

$$3CaH_4)PO_4)_2 + 6NaHCO_3 \rightarrow 3CaHPO_4 + 3Na_2HPO_4 + 6H_2O + 6CO_2 \quad (2)$$

$$3CaH_4(PO_4)_2 + 3NaHCO_3 \rightarrow 3CaNaH_3(PO_4)_2 + 3H_2O + 3CO_2 \quad (3)$$

$$3CaH_4(PO_4)_2 + 4NaHCO_3 \rightarrow Ca_3(PO_4)_2 + 4NaH_2PO_4 + 4H_2O + 4CO_2 \quad (4)$$
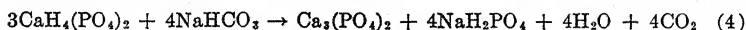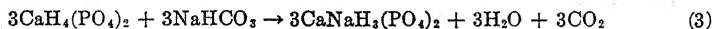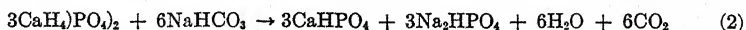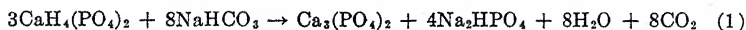
Generally the reactants are used in the proportions indicated in equation (1). The reactants are brought together in the wet dough mixture at room

temperature or lower. A reaction starts immediately but does not go to completion until the dough is subjected to baking temperature in the oven. Hart[10] claims the over-all reaction to be as in equation (1), and Patten[22] states that the reaction always results in the formation of tricalcium phosphate as one of the residual salts. The authorities generally agree on the over-all reaction but differ as to what takes place in the intermediate stages. Probably some dicalcium phosphate and monosodium phosphate are formed in the cold dough, but react further under the influence of oven heat to form more neutral residual salts.

Where monocalcium phosphate is used in combination with sodium aluminum sulfate the reactions are further complicated. In addition to the reaction possibilities indicated above there is the step of hydrolyzing the sodium aluminum sulfate ($Na_2SO_4 \cdot Al_2(SO_4)_3$) and the reaction of the resulting sulfuric acid with sodium bicarbonate. The net reaction between the sodium aluminum sulfate and sodium bicarbonate may be illustrated by the equation:

$$Na_2SO_4 \cdot Al_2(SO_4)_3 + 6NaHCO_3 \rightarrow 2Al(OH)_3 + 4Na_2SO_4 + 6CO_2$$
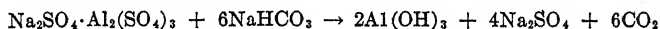
It is not at all certain that the respective baking acids in combination powders react independently with the sodium bicarbonate. Rask[23] considers it probable that the monocalcium phosphate and sodium aluminum sulfate combine in their reaction with sodium bicarbonate to yield residual salts substantially in accord with the equation:

$$Na_2SO_4 \cdot Al_2(SO_4)_3 + CaH_4(PO_4)_2 + 4NaHCO_3 \rightarrow 2AlPO_4 + CaSO_4 + 3Na_2SO_4$$
$$+ 4H_2O + 4CO_2$$
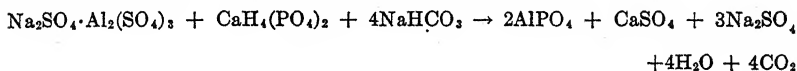
In view of the fact that the proportion of sodium aluminum sulfate in combination powders is generally much greater than that of monocalcium phosphate it is highly probable that the over-all leavening reaction involves the several reactions indicated above. It appears practically certain that during the latter part of the baking period at least some of the sodium aluminum sulfate reacts independently of the monocalcium phosphate. This is illustrated in Figure 7 (p. 455) by the side wall break in the biscuit after the dough has set.

The reaction of sodium acid pyrophosphate and sodium bicarbonate in doughs proceeds slowly at room temperature and rapidly at baking temperatures. The equation for the reaction is generally written as follows:

$$Na_2H_2P_2O_7 + 2NaHCO_3 \rightarrow Na_4P_2O_7 + 2H_2O + 2CO_2$$
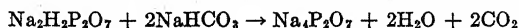
It is possible that some hydration of the sodium acid pyrophosphate takes place during the reaction with the result that part of the reaction

may proceed in accord with the equation:

$$Na_2H_2P_2O_7 + 2NaHCO_3 \rightarrow 2Na_2HPO_4 + H_2O + 2CO_2$$
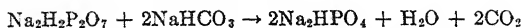
However, most authorities agree that the first equation more correctly describes the reaction.

Barackman[4] has shown that the reaction proceeds quite differently in water, biscuit doughs, and doughnut doughs at room temperature. With mixtures of sodium acid pyrophosphate and sodium bicarbonate proportioned to yield 200 cc (100 per cent) of CO_2 gas upon complete reaction, Barackman conducted rate tests using water, biscuit dough and doughnut dough at 27°C, and reported on the total CO_2 liberated, the amount retained in the dough, and that lost by escape from the dough. These data modified to show milk-type biscuits is partially presented in Table 3.

TABLE 3. VOLUME IN CUBIC CENTIMETERS OF CO_2 EVOLVED IN THE REACTION OF SODIUM ACID PYROPHOSPHATE AND SODA

Time (Mins.)	Water. Total CO_2 Liberated	Biscuit Dough (milk-type)			Doughnut Dough		
		Total CO_2 liberated	CO_2 held in dough	CO_2 lost	Total CO_2 liberated	CO_2 held in dough	CO_2 lost
½	84.3	27.0			25.6		
1	111.3	32.0			36.0		
2	120.4	47.0	17.0	30.0	40.5	4.5	36.0
4	124.2	57.5	23.0	34.5	44.7	6.7	38.0
7	125.9	64.0	29.0	35.0	48.1	9.0	40.1
10	127.6	67.5	32.0	35.5	52.0	10.5	41.5
15	129.4	70.0	34.0	36.0	56.7	12.7	43.0

The data in the above table show that the reaction characteristics of sodium acid pyrophosphate vary considerably depending on the nature of the reaction medium. These data are illustrated by the (B) curves in Figure 6.

Similar reaction rate data for monocalcium phosphate monohydrate, a commercial sodium aluminum sulfate-monocalcium phosphate combination powder and coated anhydrous monocalcium phosphate are respectively illustrated by curves (A), (C) and (D) in Figure 6.

The data show that the four designated types of baking acids react with sodium bicarbonate in distinctly characteristic manner, and that the reaction rate will vary with each type of baking acid according to the type of dough or batter in which it is employed.

The effect of the residual salts of various baking powders upon the colloidal properties of bread doughs was investigated by Smith and Bailey[25]. Variations in the ash and gluten contents of the different types of flour, such as hard and soft wheat flour, affect the alkalinity and nature of the

residual salts, the rate of gluten development, etc. These factors directly and indirectly affect the leavening reactions and baking results.

The practical value of the various leavening agents is best appraised by making actual baking tests under controlled conditions. The desired type of baked product is made by formulating definite dough mixtures with specified leavening agents, observing the action of the dough prior to the bake and evaluating the baked product.

The baking tests are made according to the standard procedure outlined by the American Association of Cereal Chemists to enable the baking expert to properly evaluate the various factors under investigation. The
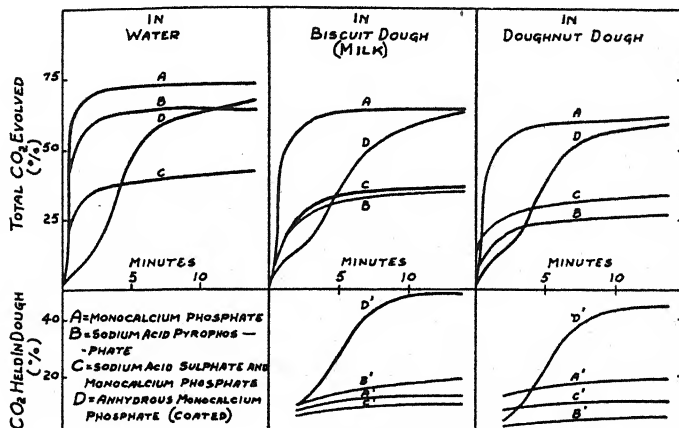
FIGURE 6. Reaction rate characteristics (at room temperature) of several baking acids mixed with sodium bicarbonate.

type of flour used in the tests should be that which is most suitable for the desired baked product.

After selecting a suitable type of flour, other ingredients, such as salt, flavoring, shortening, leavening agents, and water or milk are added and mixed to form a dough or batter. The dough is then baked and the resulting products evaluated.

Table 4 presents the results of typical baking tests using a standard biscuit formula with several types of phosphate leavening agents.

The data in Table 4 illustrate the typical differences in the baking character of the four designated phosphate containing leavening agents. No conclusions are drawn here as to which type of baking acid is best for biscuit baking, but this data in the hands of the baking expert aids him in selecting the baking acid most suitable for a particular purpose.

In addition to data of the above type the baker relies on his visual ob-

servations of the action of the dough during baking operations and other factors to aid him in his final evaluation. Observations of this type are partially recordable through use of the camera.

Figure 7 shows a series of photographs illustrating the leavening action of typical phosphate-containing baking powders at successive intervals during the baking of test biscuits. The original doughs in each case were

<div align="center">TABLE 4. BISCUIT BAKING TESTS</div>

Type of Leavening Agent	Monocalcium Phosphate (Monohydrate)	Monocalcium Phosphate (Coated Anhydrous)	Sodium Acid Pyrophosphate	Sodium Aluminum Sulfate[40] Plus Monocalcium Phosphate[40] (Monohydrate)
Neutralizing value	80	83.4	71.5	90
Soda level (% of flour)	1.5	1.25	1.5	1.5
Type of dough	Harsh and short	Soft and smooth	Very soft and smooth	Slightly harsh and slightly short
Weight of 7 doughs (grams)	222	240	237	239
Height of 6 biscuits (inches)	$7\frac{1}{2}$	10	$8\frac{1}{2}$	$8\frac{1}{2}$
Specific volume of biscuit:				
(a) on wt. of dough (expansion)	2.02	2.58	2.11	2.24
(b) on wt. of biscuit (lightness)	2.42	2.81	2.65	2.56
Crumb color	White	Very white	Creamy white	White, slightly creamy
pH value of crumb	7.25	7.25	7.8	7.5
Biscuit side wall	Slight split	Smooth	Smooth	Deep split

formulated on a uniform sodium bicarbonate basis. The top row illustrates the action of sodium acid pyrophosphate. It will be noted here that the leavening action is substantially complete by the time the dough is set, resulting in biscuits having smooth side walls. The second row shows the use of a sodium aluminum sulfate-monocalcium phosphate combination powder. The photographs show that a considerable amount of leavening gas is liberated after the dough is set resulting in a deep split biscuit. The third row illustrates the use of monohydrated monocalcium phosphate. The bottom row indicates the action of coated anhydrous monocalcium phosphate. Here it will be observed that the leavening action is substantially

completed at the end of 4 minutes, before the dough has set, and that biscuits with smooth side walls are obtained.

Baking Powders

Baking powders as we know them today are defined[26] as "the leavening agents produced by the mixing of an acid-reacting material and sodium bicarbonate with or without starch or flour. It yields not less than 12 per
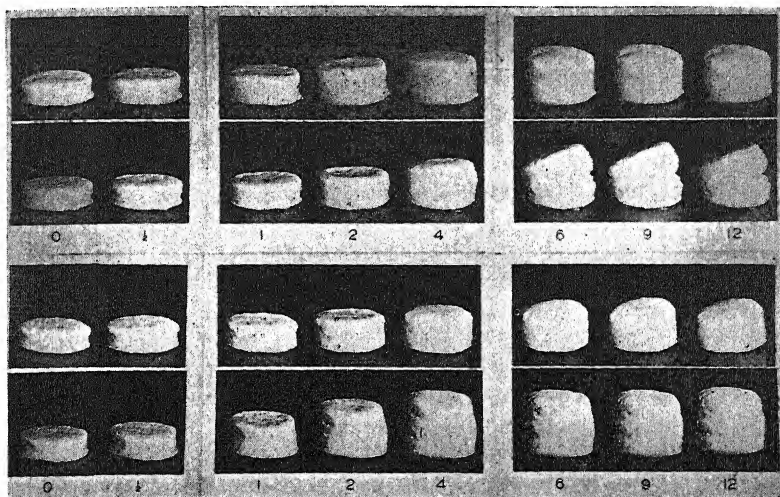
Figure 7. Photographs of biscuits at different intervals (minutes) during the baking operation. Top row—Sodium acid pyrophosphate is employed. Second row—Combination of sodium aluminum sulfate and monocalcium phosphate is employed. Third row—Monohydrate monocalcium phosphate is employed. Bottom row—Coated anhydrous monocalcium phosphate is employed.

cent of available carbon dioxide". This definition permits considerable leeway in selection of the acid ingredient. For purpose of the present discussion only the monocalcium phosphate and sodium acid pyrophosphate type baking acids will be considered.

In view of the fact that baking powders contain both acid and basic reactants it is necessary to use extreme care in the selection and mixing of the components in order to avoid premature reaction and loss of carbon dioxide under normal storage conditions. In most cases the sodium bicarbonate and the phosphate baking acid are in granular form. This reduces the surface contact between the reactants. Cornstarch is also included as an inert component of the mixture to coat the reactant particles and further reduce their points of direct contact. The starch also serves as a

filler which enables the manufacturer to formulate the powder so that a standard amount of available carbon dioxide is present per unit weight of baking powder. The standard practice is to formulate the mixtures so that the freshly prepared powders will contain approximately 14 per cent of available carbon dioxide.

Phosphate containing baking powders are of two general types, namely, straight phosphate powders and combination powders. Straight phosphate powders contain monocalcium phosphate as the sole acid ingredient, whereas combination powders contain both monocalcium phosphate and sodium aluminum sulfate. Perhaps baking powder containing coated anhydrous monocalcium phosphate should be defined as a special straight phosphate powder because of its different reaction rate character. A straight phosphate powder containing the ordinary monocalcium phosphate monohydrate will liberate approximately two-thirds of its leavening gas during the dough-mixing stage. A large proportion of this gas escapes from the dough and is not available for leavening purposes. With straight phosphate powders containing the coated anyhdrous monocalcium phosphate less than one-fourth of the leavening gas is lost in the dough mixing stage, leaving most of the leavening gas to be liberated in the early part of the baking period. With combination powders the monocalcium phosphate monohydrate causes generation of a portion of the leavening gas in the dough-mixing stage while the sodium aluminum sulfate component of the powder reacts more slowly resulting in liberation of a large proportion of the leavening gas in the baking stage.

Table 5 shows the analyses and general baking quality of a number of straight phosphate and combination baking powders found on the market. The shelf life history of these powders is unknown but none has deteriorated sufficiently to prevent them from being considered typical of the various baking powders available to the housewife.

Baking powders containing sodium acid pyrophosphate, while quite popular in Europe, have found little favor in this country for household use. Their principal use in this country is in the manufacture of high strength baking creams and powders for the cake making industry. A baking cream is usually prepared by mixing a sufficient amount of corn starch with sodium acid pyrophosphate to bring the neutralizing strength to about that of cream of tartar, namely, 50 per cent. Such baking creams are sold to the baker who mixes them with sodium bicarbonate in the proportion of two to one by weight.

Baking powders are sensitive to moisture and should be kept where possible in closed containers in a dry atmosphere. Under normal storage conditions baking powders slowly deteriorate due to absorption of moisture from the air permitting a slow reaction between the baking acid and the

Table 5. Composition and Properties of Several Typical Phosphate-Containing Baking Powders Found on the Market

	A	B	C	D	E	F	G
Approx. Composition							
Sodium bicarbonate	27.2%	27.0%	28.0%	30.1%	28.2%	31.2%	28.4%
Monocalcium phosphate	34.0	31.5	10.7	6.2	12.7	13.4	33.8
Sodium Alum. sulfate			21.4	27.6	19.5	22.1	
Starch	38.8	41.5	39.9	36.1	39.6	33.3	37.8
	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Type of monocalcium phosphate used	Hydrate gran.	Hyd. gran.	Hyd. gran.	Hyd. powd.	Hyd. gran.	Hyd. powd.	Anhydrous coated
Sodium bicarbonate	Gran.	Gran.	Gran.	Powd.	Gran.	Powd.	Gran.
Analyses							
Total CO_2	14.0%	13.9%	14.4%	15.5%	14.5%	16.1%	14.9%
Residual CO_2	0.5	0.6	1.1	0.8	0.7	1.0	0.4
Available CO_2	13.5	13.3	13.3	14.7	13.8	15.1	14.5
P_2O_5	18.8	17.4	5.9	3.4	7.0	7.4	20.1
SO_3	None	None	14.1	18.2	12.9	14.6	None
Biscuit baking tests (1.5% soda level)							
Ht. of 6 biscuits (in.)	7½	8	8¼	8¼	8	8½	10½
Wt. of 7 doughs (gram)	199	205	228	225	213	208	234
Vol. of 7 biscuit (cc)	410	450	510	470	450	440	605
Spec. vol. (biscuit wt.)	2.42	2.58	2.60	2.42	2.44	2.52	3.0
pH of crumb	7.3	7.8	8.15	7.5	7.9	8.2	7.35

sodium bicarbonate. The average shelf life of baking powders is approximately one year, before the amount of available carbon dioxide is reduced below the 12 per cent legal limit. In air-tight containers the life of a properly prepared baking powder may sometimes be extended for several years.

Self-Rising Flour and Prepared Mixes

In the Federal Register of October 30, 1948, the Food and Drug Administration in paragraph 15.50 defines self-rising flour as follows:

"Self-rising flour, self-rising white flour, self-rising wheat flour, is an intimate mixture of flour, sodium bicarbonate, and the acid-reacting substance monocalcium phosphate or sodium acid pyrophosphate or both. It is seasoned with salt. When it is tested by the method prescribed in paragraph (c) of this section not less than 0.5 per cent of carbon dioxide is evolved. The acid-reacting substance is added in sufficient quantity to neutralize the sodium bicarbonate. The combined weight of such acid-reacting substance and sodium bicarbonate is not more than 4.5 parts to each 100 parts of flour used."

A typical general purpose self-rising flour may contain 1.5 lbs of sodium bicarbonate, 1.87 lbs of monocalcium phosphate (monohydrate) and 2.0 lbs of salt per 100 lbs of flour. By substituting coated anhydrous monocalcium phosphate for regular monocalcium phosphate the formula would change to 1.25 lbs sodium bicarbonate, 1.50 lbs coated anhydrous monocalcium phosphate and 2.0 lbs of salt per 100 lbs of flour.

With other types of prepared mixes such as pancake, waffle, and special self-rising flour mixes the flour is usually blended to include other types of flours such as corn flour, soya flour, rice flour, buckwheat flour, etc. The baking powder ingredients, flavoring, etc., are varied according to the results of numerous baking tests conducted in the service laboratories of the different manufacturers of such mixes. Some manufacturers add powdered buttermilk, dried skim milk, or corn sugar to their pancake mixes, in quantities up to 5 to 7 per cent, in order to produce the golden brown color on the surface of the cake and make it more attractive and palatable.

It is generally necessary to increase the amount of leavening agent in pancake and waffle mixes as compared to plain self-rising flour because of the different character of the batter and baked goods. A typical pancake flour will contain about 1.75 to 2.00 lbs of sodium bicarbonate and 2.0 to 2.30 lbs of the baking acid per 100 lbs of flour.

As in the case of regular baking powder compositions it is necessary in self-rising flour mixtures to maintain a correct balance between the baking acid and sodium bicarbonate in order to avoid the disadvantages of alkaline or acidic residual salts in the baked product.

In the preparation of self-rising flours the acidic phosphate salts are

thoroughly mixed with the flour before adding the sodium bicarbonate. This avoids unnecessary direct contact of the reactants and results in a stable self-rising flour product having a long shelf life. Under normal storage conditions the leavening ingredients will retain their baking efficiency as long as the flour itself remains sound.

Phosphated Flour

Phosphated flour is defined as plain flour to which from 0.25 to 0.75 per cent monocalcium phosphate has been added[8]. The practice of adding monocalcium phosphate to all-purpose family flour was started in the south about 30 years ago primarily to offset undesirable alkaline conditions in baked products generally resulting from the use of too much soda when making sour milk biscuits, etc. It has since been found that the added phosphate has several other advantages. It has a desirable conditioning effect on the gluten yielding a softer and more plastic dough, and prevents "rope development" in yeast doughs made from such flours. It is also claimed that the extra calcium and phosphorus has an important health advantage.

Today, more than two-thirds of the all-purpose family flour sold in the south contains added phosphate. This phosphate is generally added in the form of finely divided monocalcium phosphate monohydrate or anhydrous monocalcium phosphate. The amount normally included is about 0.5 per cent of the hydrated or 0.4 per cent of the anhydrous type phosphates.

Flour enrichment has become an important factor in recent years. Standards adopted by the Food and Drug Administration[8] provide that each pound of enriched flour shall contain from 2.0 to 2.5 mg of thiamine, 1.2 to 1.5 mg of riboflavin, 16.0 to 20.0 mg of niacin or niacinamide, and 13.0 to 16.5 mg of iron. Enriched flours to which calcium is added as an optional ingredient must contain from 500 to 625 mg of calcium (Ca) per pound of flour. To meet this requirement for enriched phosphated flours the phosphate manufacturers have developed a special grade of high calcium containing monocalcium phosphate. This product is essentially a monocalcium phosphate containing dicalcium phosphate, in which the ratio CaO to P_2O_5 is approximately 0.5 Such a product when added to flour in the amount of 0.5 per cent will supply the necessary calcium (500 mgs/lb flour) to meet the calcium enrichment definition.

"Rope" development in yeast leavened bread is a disease due to the activity of some form of *Bacillus mesentericus* infection of the flour[9]. It is effectively controlled or prevented by including monocalcium phosphate in the flour used for making the yeast leavened doughs. When a serious infection develops it may be necessary to employ as much as 0.5

per cent of monocalcium phosphate to prevent rope development in the bread, until the source of infection is located and eliminated.

Cake making is a highly specialized field, and for optimum results it is necessary to select critically both the type of flour and type of leavening agents to be employed. Normally cake batter is relatively thin and is not appreciably aerated before placing the batter in the oven. In view of this condition, the type of baking acid used should be one which has a delayed or slow reaction rate with sodium bicarbonate during the batter-mixing period. Sodium acid pyrophosphate is most generally used for this purpose. Coated anhydrous monocalcium phosphate is quite suitable for cake making, especially in the home where only small volumes of batter are handled at one time.

Bread Improvers

Bread improvers, many of which contain a phosphate component, are employed extensively by large commercial bakers to improve the quality of yeast-leavened products. The so-called bread improvers generally include ammonium and calcium salts to stimulate growth of the yeast cells. Small amounts of bromates or iodates, etc., are generally included in the compositions to decrease the proteolytic action of the enzymes natural to flour and yeast, and thus prevent softening of the doughs during processing in the bake shop.

The calcium salt generally used for this purpose is monocalcium phosphate. A typical bread improver composition is illustrated by the following formula:

	(%)
Ammonium sulfate	7.5
Monocalcium phosphate	50.0
Potassium bromate	0.3
Salt	20.0
Starch	22.2

From 0.25 to 0.5 per cent of such composition added to flour will give noticeably improved results in the production of yeast leavened bread.

Nutritional Value

No inorganic element plays such a vital and complex role in the structure and functions of the human body as the element phosphorus. The bones, muscle tissues, nerve cells, etc., require new supplies daily of assimilable phosphorus compounds. Such compounds must be supplied in the diet. V. K. LaMer[15] gave an excellent summary of the literature and presented experimental evidence showing that calcium phosphates having a Ca to P ratio between 1:1 and 2:1 are the most readily available forms of these

elements in the diet. LaMer and others[21] have demonstrated the necessity of maintaining a balanced relation between the calcium and phosphorus intake even though the functional processes of the body seem to concentrate the calcium in the bones, whereas the muscle tissues, nerve cells, etc., utilize complex organic phosphorus compounds synthesized in the body processes.

FUTURE TRENDS

In view of the improvements in the quality and baking characteristics of the chemical leavening agents in the past decade or so, it is expected that further improvements will be made in the future particularly in the keeping quality and reaction rate characteristics of the baking acids. It is not likely that the trend will be away from phosphate types because of their inherent value from the nutritional standpoint. Prepared flour mixes, including correctly proportioned leavening agents and other nutritionally desirable additives probably will tend to supplant the plain family flour, because of the ease with which the housewife may make the perfectly leavened baked products by simply mixing the flour with water and shortening to form the dough.

Progress and development in the field of leavening agents has been paralleled by the issue of patents covering the more important improvements, and for those who wish to make a more complete study of the art a list of the United States patents pertaining to phosphorus compounds related to the baking industry is included in Table 27 in the Appendix. The assistance of Mr. W. A. Vater in the preparation of this list is greatly appreciated.

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24. Phosphate Water-Softening and Cleansing Products

C. Rogers McCullough

Monsanto Chemical Company

Practically all natural waters contain impurities in varying amounts. These impair their value for industrial uses such as boiler feed water, city supplies of potable water, in laundering, and for the textile and various other chemical industires. The sodium salts of orthophosphoric acid and their derivatives, the metaphosphates, pyrophosphates and the so-called polyphosphates are playing an increasingly important role in the treatment of water for these various purposes.

The commonly occurring dissolved salts which render the water hard are the bicarbonates, carbonates, sulfates, chlorides and nitrates of calcium and magnesium, and the sulfates of iron and aluminum[1]. Silica is also found in many waters and becomes important especially in the case of boiler feed water. It does not contribute to hardness but it does form boiler scale and is an important cause of turbine fouling. The removal of these impurities is called water-softening, and this operation is carried out by industries, residences, and municipalities.

The suspended material is removed by coagulation, settling and filtration. Bacteria are destroyed by chlorination or other processes. The dissolved salts are removed by a variety of processes in some of which phosphates play an important role. Schwartz and Munter[133] give an excellent review of the role of phosphates in water softening. The various phosphates used for this purpose, their functions and the methods employed in manufacturing them are described and discussed in this chapter.

Treatment of Boiler Waters

Some years ago, and even today in a number of primitive and small boiler installations, certain natural waters could be fed to the boilers without serious consequences. However, in the present large installations for industrial and public utility use, and even for locomotives, it is desirable and often necessary to treat the water before feeding it to the boiler. The use of water improperly treated will result in the build-up of scale on the heat-transfer surface which acts as a heat insulator[35] resulting in losses of

efficiency of 7 to 16 per cent[17]. In modern boilers the rate of heat transfer is so high that the deposition of scale will cause overheating of the boiler tubes and subsequent blistering and rupture. Boiler waters are also treated to avoid cracking and corrosion. The proper treatment of boiler water is a complex subject with an extensive literature as each natural water and each boiler installation has individual requirements. Those interested in this general problem should consult the work of R. E. Hall et al.[42, 53, 109], dealing with scale formation and boiler-water treatment and the study by Schroeder and Berk[131] on boiler cracking.

Internal Treatment

When the steaming rate of a boiler is comparatively low or the available natural water is low in hardness it is feasible to add treating chemicals directly to the raw feed water and allow the precipitation of salts to occur inside the boiler. Phosphates[44, 122] are generally used because they reduce the solubility of the scale-producing ions to a very low figure, they control pH, and form flocculent precipitates which remain suspended and removable in the boiler blow-down. Phosphates have been used in boiler treatment since 1886[82].

Di- and trisodium phosphate probably react with the salts of calcium, magnesium and iron to form insoluble phosphates according to the following reactions:*

$$3CaCO_3 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 3Na_2CO_3 \tag{1}$$

$$3MgSO_4 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 3Na_2SO_4 \tag{2}$$

$$FeCl_3 + Na_3PO_4 \rightarrow FePO_4 + 3NaCl \tag{3}$$

$$3Ca(HCO_3)_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaHCO_3* \tag{4}$$

$$Ca(HCO_3)_2 + Na_2HPO_4 \rightarrow CaHPO_4 + 2NaHCO_3* \tag{5}$$

$$CaSO_4 + Na_2HPO_4 \rightarrow CaHPO_4 + Na_2SO_4 \tag{6}$$
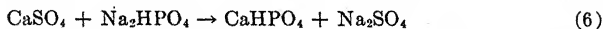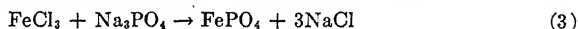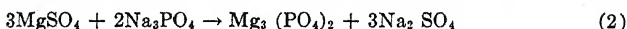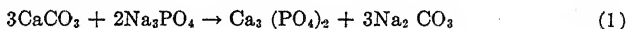
Trisodium and disodium orthophosphates are used in a large number of the patented boiler compounds[106]. Various combinations have been proposed such as the addition of ammonium salts[32]; caustic soda[110]; complex

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* The calcium phosphate precipitate, reaction (1), is usually written $Ca_3(PO_4)_2$ even though the precipitate is probably calcium hydroxy apatite $[Ca_3(PO_4)_2]_3 \cdot Ca(OH)_2$. In reactions (4) and (5) the $NaHCO_3$ breaks up to give Na_2CO_3 water and CO_2, the CO_2 passing off in the steam. Some break down of Na_2CO_3 to $NaOH$ and CO_2 also occurs, the amount depending on temperature and composition of the solution.

It is doubtful if $FePO_4$ or $CaHPO_4$ are ever present in the sludge of operating boilers. These compounds will react to form iron hydroxides and hydroxyapatite respectively.

silicates[30, 83]; a mixture of sodium amalgam, tannin, kerosene, whale or seal oil, and sodium hydroxide[7]; sodium carbonate, lime, sodium silicate, caustic soda, and sodium bichromate[19], soap[33], sodium carbonate, dextrin or starch, and cutch (a substance obtained from the bark of Mangrove trees) to yield tannic acid[5]; various acidic substances, e.g., H_3PO_4, H_2SO_4, H_3BO_3[68]; sodium carbonate and starch, to one or more phosphate salts[141]. These compositions are all claimed to have various advantages such as lack of priming (ejection of water from the boiler along with the steam), non-adherence of scale[141], prevention of embrittlement[107], and reduction of foam, as well as supension of the precipitates and the elimination of scale deposits on the heating surfaces.

Phosphate Sequestering Agents

When phosphates are added to the feed water line the calcium and magnesium phosphates precipitate immediately and cause blocking of the line. Hall and Jackson[46] patented the use of molecularly dehydrated phosphates for addition to the feed water. Glassy sodium metaphosphate forms soluble complexes with calcium and magnesium compounds, keeping these in solution so that the addition of carbonate, orthophosphate or soap does not produce a precipitate. This action of sodium metaphosphate is termed sequestering and is usually written as follows:

$$Na_6(PO_3)_6 + Ca^{++} \text{ ions} \rightarrow Na_4 \, Ca \, (PO_3)_6 + 2Na^+$$
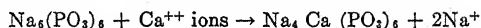
Actually, the structure of glassy sodium metaphosphate is not known[108], nor is the sequestering reaction thoroughly understood. The ratio of metal phosphate (PO_3) to the ions being sequestered (calcium, magnesium, iron, etc.), varies somewhat with concentration, pH, and the character of the metaphosphate or polyphosphate groups. Phosphates other than metaphosphates have the power to sequester. For example, Hall[45] has patented the use of molecularly dehydrated phosphates and specifically mentions pyrophosphates as addition agents for boiler feed water. He also discloses the use[47] of pyrophosphates as a means of holding magnesium ions in solution in a non-ionic form without substantially sequestering calcium ions so that the water may be passed through a zeolite for the preferential removal of calcium ions.

Various phosphate sequestering agents are described and compared by Gilmore[39], Rudy et al.[126], Huber[67], Durgin et al.[31], Corsaro[24], Jackson[70], and Hatch[62]. Phair[111] in his book on "Colloid Chemistry" discusses the sequestering action of polyphosphates on calcium and magnesium. Further discussion of these polyphosphates, especially in connection with washing operations are given by Mann and Ruchhoft[91]. Methods of making monomeric and polymeric sodium triphosphate are described in patents issued to King[78].

Under the high-temperature conditions existing in the boiler the *meta* of other complex phosphates reacts with water and reverts to orthophosphates which react with the calcium and magnesium, (or other ions causing hardness), to form precipitates. The reversion of metaphosphates also neutralizes alkalinity since the orthophosphates formed are acidic. The reaction can be simply written.

$$(NaPO_3)_n + nH_2O \rightarrow nNaH_2PO_4$$
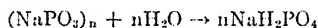
External Softening

Generally speaking, the larger and more modern boiler installations soften the water externally to the boiler to a large extent. The commercially used systems are the lime-soda, both hot and cold, and the ion-exchange or zeolite type softeners, and sometimes phosphate[73, 90]. The effluent from these softeners is practically always treated with phosphates (generally meta- or polyphosphates) since, there is usually a small amount of hardness remaining when the softener is in normal operation. The phosphates also provide a safety factor for accidental entrance of raw water, a necessary precaution with modern high rating boilers.

Hot lime-soda softeners can be obtained with guarantees of 25 ppm of hardness as calcium carbonate (1.2 grains per gallon) using excess soda ash of 1.5 grains per gallon but theoretically and in actual operation the hardness can be reduced to 10 to 15 ppm (0.6 to 0.9 grains per gallon[81]) or perhaps lower in certain cases by carrying a greater excess of soda ash. In the case of cold lime-soda softeners sometimes hardness values of 51 ppm are obtained in the effluent, and sodium phosphate and caustic soda are added to correct for this[72].

Reigner[116] has discussed the lime-soda softener and believes that theoretical reduction of hardness is not reached because of the sub-microscopic particles of $CaCO_3$ remaining in the water. Lime-soda and zeolite softeners are used to remove the bulk of the hardness before adding phosphates in order to reduce cost, as pointed out by Weiss[150]. Zeolites or ion-exchange resins may be used in place of the soda-lime treatment in the preliminary softening of water. These ion-exchange systems can be arranged so as to remove all ion constituents and produce the equivalent of a distilled water containing a few parts per million of dissolved substances, but the cheaper ion-exchange systems which remove calcium, magnesium, aluminum and iron ions and replace them by sodium ions are more generally used. Under these conditions the total amount of material dissolved in the water is not appreciably changed.

In a typical ion-exchange installation for a 675 psi boiler, treating a raw water containing approximately 130 ppm of dissolved calcium and magnesium chiefly as sulfate, the raw water passes through the following steps:

The ion-exchanger removes the calcium and magnesium ions replacing them by sodium ions. The water is then passed through a deaerator-heater operating at 220°F and CO_2 and oxygen are removed as far as possible. Then a small amount of sodium sulfite solution is added to combine with any residual oyxgen. The water is then treated with a small amount of a solution of glassy sodium metaphosphate and caustic soda to adjust the boiler water alkalinity to about 200 ppm as hydroxide, and then pumped into the boiler. In normal operation this boiler has a continuous blow-down of approximately 8 per cent of the feed water so as to maintain the total solids in the boiler water at 1800 to 2200 ppm. The boiler water contains suspended matter, mostly calcium phosphate and magnesium silicate (serpentine) to the extent of 30 to 40 ppm. Serpentine is preferred over magnesium phosphate as a precipitate since it adheres less. Under these conditions this boiler operates continuously without any scale deposition on the heating surfaces.

High-Pressure Boiler Operation

When boilers are operated at 200-pound pressure and above, any sodium carbonate dissolved in the water decomposes to liberate CO_2 which goes off in the steam leaving sodium hydroxide in the boiler water[53]. Excess alkalinity, however, has been recognized as a cause of intergranular corrosion and cracking at highly stressed areas of the boilers[131] and means must be taken to keep the caustic alkalinity within certain limits[80, 114].

It is necessary for boilers operating at 700-pound pressure or above to have feed water practically completely deaerated, of zero hardness and with an accurate control of pH and total solids. These factors are discussed by Sitter and Massey[136]. Records are available for the operation of boilers at 1700-pound pressure for a period of years using phosphate treatment successfully [151]. There are a number of careful studies of the equilibrium conditions within the boiler by Clark *et al.*[20], Ammer[2], Kostrikin[79], and by Schläpfer and Lehner[130]. An excellent review of the progress which has been made in the design and operation of boilers chiefly on account of the use of phosphates is given by Partridge and Purdy[109]. Potassium phosphates, as well as sodium phosphates, have been used for boiler-water treatment as described by Berk and Rogers[10] and Hankinson and Baker[54]. See also the basic patent by Hall[51] on the use of potassium salts for boiler conditioning. Various means of supplying polymeric phosphates to boiler water are described by Hall and Jackson[46], Bird[12], Wilson[152], King[76], Smith[139], Durgin *et al.*[31], Taylor[143], and Hall and Munter[50]. The advantages of these substances are convenience in handling, ability to prevent immediate precipitation of calcium and magnesium, and their control of alkalinity by hydrolysis to more acidic phosphates in the boiler.

Marine boilers are a special case since they are designed for very high rates of steam generation per unit of surface. These boilers are usually fed with distilled water, but even in this case, phosphates are customarily added to the feed water, as described by Purdy[115], as insurance against scale formation.

<div align="center">THRESHOLD TREATMENT OF WATER</div>

Suppression of Calcium Carbonate Deposition

In the process of adding ammonia to irrigation water for fertilizer purposes the resultant alkalinity ordinarily causes the precipitation of calcium carbonate. Rosenstein[29, 124] found that the addition of 1 ppm of a soluble metaphosphate prevents this precipitation. This interesting phenomenon has been studied quite extensively by Rice and Partridge[120] who showed that 1 to 5 ppm of glassy sodium metaphosphate prevent precipitation in bicarbonate waters used in cooling systems and heat exchangers; they also prevent the after-precipitation of calcium carbonate in water from lime-soda softeners[11]. The authors believe that this so-called threshold method is superior to all others that have been tried heretofore. This method is used quite extensively to avoid deposits in engine cooling systems as described by Mathews[93], Yetman[153], and Simons[135]. Fink and Richardson[34] describe the addition of polyphosphoric acid to boiler feed water in quantities not exceeding 9 ppm. Air conditioning systems also have scale and corrosion problems and in these glassy metaphosphates and polyphosphates are used effectively[128]. A study of the mechanism indicates that apparently the polymeric phosphate ions are strongly adsorbed on the embryonic crystals of calcium carbonate and inhibit their further growth[120].

Corrosion Inhibition

It was also found that these ions are adsorbed on metal surfaces and inhibit corrosion. As a result of these discoveries a number of municipal softening plants have utilized glassy sodium metaphosphate to prevent the deposition of calcium carbonate in the filter beds and pipelines subsequent to lime-soda softening[65, 121, 134]. Rice, Partridge and Hall[118] claim not only prevention of deposits and corrosion by the threshold treatment, which they define as 1 to 2 ppm of glassy sodium metaphosphate, but also the gradual solution of old scale. Hall[52] calls glassy sodium metaphosphate the cinderella of the phosphates, and points out that it suppresses the ionization of many metallic salts in solution, coagulates albumin, has a high dispersive action, and stabilizes supersaturated solutions of calcium salts, especially calcium carbonate. There are a number of other publications describing in detail experiences with sodium metaphosphate in various municipal water systems[3, 6, 23, 25, 37, 41, 103, 119, 123, 129, 138, 142, 146, 154]. Moore[98]

and Pallo[105] however doubt the effectiveness of metaphosphate in preventing or reducing corrosion. Navet[102] described experiments showing that the hexametaphosphate (glassy metaphosphate) ion forms stable complex compounds with iron in the presence of sodium carbonate, ammonium hydroxide, and sodium hydroxide. By the use of 5 ppm of glassy sodium metaphosphate and adjustment of the pH to 10 to 11 by sodium carbonate, a mineral water containing 21 ppm of iron was stabilized so that no iron or manganese precipitated for a period of two months. This author also claimed that the metaphosphate inhibited the oxidation H_2S and the evolution of CO_2.

McCarthy and Cassidy[94] found that the addition of phosphates to raw water increases the rate of bacterial growth. The increase of growth is enormous with metaphosphate and it is recommended that sodium hypochlorite be added along with the metaphosphate when treating potable waters. Orthophosphate gives a smaller increase and pyrophosphate gives the least increase in rate of growth of bacteria. Ingleson and Thomas[69] report that 2 ppm of glassy sodium metaphosphate decreased the amount of iron deposited in the distribution lines but not in the hot water systems. Hatch and Rice[61] noted that in order to stabilize iron in waters, the metaphosphate must be added before the iron-bearing water is exposed to air or chlorine. Calgon, Inc., and Albright & Wilson[18] patented the use of "Calgon" (metaphosphate) to prevent the build-up of soft hydrated Fe_2O_3 in water pipes. "Calgon" must be added before the water is exposed to air or treated with chlorine or other oxidizing agents.

Morgan and Swoope[100] and Kehren[74] studied the rates of hydration of commercially available pyro-, meta- and tetraphosphates to provide data on their useful life for corrosion inhibiting purposes in water-treatment. They found that the useful life is increased when the pH is maintained between 7 and 9. Higher temperatures increase the rate of hydration. Bell[8] made a careful study of hydration rates of dehydrated sodium phosphates. The Water Pollution Research Board of Great Britain made a review, July 1, 1939 to December 1, 1945[4], covering the whole subject of water treatment, including the use of phosphates, especially hexametaphosphates. Attempts have been made to prepare compositions of metaphosphate which are slowly soluble or have a low equilibrium concentration to obtain the desired value in water. One example is a glassy composition containing metaphosphate and Al_2O_3[77].

Before the threshold treatment using sodium hexametaphosphate was discovered, other means of preventing the after-precipitation of calcium carbonate had been used. One interesting procedure was employed on a large scale at Columbus, Ohio[64], where phosphoric acid was added at the rate of 0.7 grains per gallon of water leaving the lime-soda softener. This

gave a fully carbonated water and a material reduction in residual hardness. McMurtie[96] disclosed the use of phosphoric acid or acid phosphate to treat sewage sludge. The soaps and carbonates present are decomposed and a flocculent precipitate of dicalcium phosphate is formed which carries down the solid or suspended matter much of which contains nitrogen. It was proposed that the settled residue be used as a fertilizer but little has been done on this process in a commercial way.

Treating Water for Cleansing

There is a similarity between the problems of softening water for commercial laundries and for boiler use. In both instances it is desired to remove from solution the calcium and magnesium compounds. In the case of boilers, the water is softened to avoid scale deposits on the boiler tubes and reduction of efficiency; in the case of laundries the water is softened to avoid reaction of the calcium and magnesium ions with soap to form sticky precipitates or curds.

Soap Saving

The formation of soap curds results in the waste of soap and also in imperfect cleansing of the cloth because of the adherence of the curd and the formation of streaks and stains. The deposition of soap curd on cloth is also supposed to shorten its life and often gives rise to objectionable odors due to the development of rancidity. The saving in soap which may be effected by reducing the hardness of the water is shown in Table 1[113].

Trisodium phosphate was one of the first phosphates used for softening water to be used for cleansing. Calcium and magnesium are precipitated as the phosphates and this avoids precipitation of soap curd. Moreover, the alkalinity of the water is increased, which is generally desirable for the neutralization of acidity in soiled clothes. It is customary for large commercial laundries to use water softeners either of the lime-soda, or ion-exchange type. The ion-exchange type is becoming increasingly popular because of the simplicity of operation. Subsequent to the softener various materials are added such as souring agents, bleaches, soap, soap builder, synthetic detergents, etc. Modern laundry practice has become a highly complex subject and the detergent mixtures used depend upon the type of clothes being washed, kind of water available, and the economics and availability of various detergent compounds. In an investigation of detergency Oesterling[104] and Harris and Brown[58] studied the additive effect of $NaOH$, Na_3PO_4, $NaHCO_3$, Na_2SiO_3, and Na_2CO_3, as supplements to soap.

Soap Builders

Harris[59] describes the effect of phosphate soap builders on the detergent efficiency of synthetic detergents of the dodecyl-benzene-sulfonate type.

He showed that tetrasodium pyrophosphate is one of the best all-around builders for this purpose. These mixtures are particularly good for sea water. The same author[56] stated that tetrasodium pyrophosphate is an excellent builder for soap.

Rhodes and Winn[117] studied the detergent action of soap in the presence of chlorides, sulfates, and phosphates and found that at the optimum pH, additions of salts increase and then decrease the detergent effect. The effect of the added salt is proportional to the valence of the anion. Curtis[28] patented a dry detergent mixture consisting of soap powder, Na_3PO_4 or

TABLE 1. SAVING OF SOAP EFFECTED BY LAUNDRIES USING SOFTENING PROCESSES

Name and Location of Laundry	Hardness	Quantity of Soap Used (lbs)		Saving of Soap (%)
		Without Soften'g	After Soften'g	
	Grains per gal.			
Snow White Laundry, Wilmington, Del.	3½	400	150	62
City Star Laundry, Harrisburg, Pa.	5	772	318	59
American Laundry, Grand Rapids, Mich.	7	973	350	64
Walker's Laundry, Niagara Falls, N. Y.	7	400	96	76
Yale Laundry, Washington, D. C.	7	621	255	59
Kennedy Laundry, Chicago, Ill.	8	1,872	671	64
Olean Palace Laundry, Olean, N. Y.	9	170	48	72
Westminster Laundry, St. Louis, Mo.	9	750	250	66
Cascade Laundry, Great Falls, Mont.	10	580	153	73
Imperial Laundry, Albuquerque, N. M.	10	800	132	83
Crown Laundry, Indianapolis, Ind.	19	954	502	47
Perfection Laundry, Springfield, Ohio	20	682	224	67
Average				66

Na_2CO_3, and a silica aerogel, for which is claimed anti-caking and emulsifying action.

In the 1930's metaphosphates, pyrophosphates and various polyphosphates became available and a variety of studies were made of the effectiveness of these materials as water-treating agents and builders for soap. Hall[47] patented the use of $NaPO_3$ using a mole ratio to calcium compounds of at least four. Lindner[85] studied the effect of organic detergent watersofteners versus metaphosphates in the presence of soap in hard waters. Metaphosphate actually softens the water and has the power to dissolve dried calcium soaps. Gilmore[39] and Treffler[146] compared sodium metaphosphate and tetrasodium pyrophosphate at pH 10 in dissolving calcium phosphate precipitate in the presence of soap. They concluded that sodium metaphosphate is more effective on a weight basis than pyrophosphate. At higher temperatures metaphosphate decomposes slowly in neutral solu-

tions and more rapidly in alkaline solutions, whereas pyrophosphate is unchanged during boiling and its softening and detergent strength are improved by alkali.

Hatch and Rice[60] claimed that hexametaphosphate has surface-active properties in addition to its water-softening values. Gillet[38] compared meta-, pyro-, and orthophosphates and pointed out that the metaphosphates sequester calcium and magnesium, the pyrophosphates have a powerful peptizing and a marked specific solvent action on certain gums and resins, and the orthophosphates are good water softeners.

Tetrasodium Pyrophosphate

Tetrasodium pyrophosphate is an important component of soap powder compositions and Cobbs et al.[21, 22, 57] claimed that it increases the effectiveness of other detergents because of its combined emulsifying and water-softening properties. Morrisroe and Newhall[101] studied the effect of phosphate builders on the effectiveness of synthetic detergents and soap and concluded that tetrasodium pyrophosphate was superior to trisodium phosphate for this purpose.

During World War II fats and oils were very scarce and synthetic detergents moved forward rapidly. Synthetic detergents are not the equal of soap for the removal of heavy soil, particularly from cotton fabrics, unless built with phosphates. Hersberger and Neidig[63] reviewed the status of synthetic detergents subsequent to the war when oil and fat prices were returning to normal and concluded that synthetic detergents built with tetrasodium pyrophosphate are as good as built soaps and will continue to be used. They found in their study that sodium tripolyphosphate is equally good or slightly better than pyrophosphate.

Bowman[15] discussed the properties of pyrophosphate and described the non-ionized salts which are formed by pyrophosphates when present in excess in solutions of Mg, Fe, Al, Mn, Zn, Cr, Cu, Ni, Ba, Sr. Vallance[147], Janota and Hull[71], Vaughn and Vittore[148], reviewed the application of pyrophosphates in soap and allied industries. Kepfer[75] claimed increased water softening effect by dissolving tetrasodium pyrophosphate in hot water and then adding sodium metasilicate or disodium phosphate prior to precipitation of the hardness. Skeen[137] reported that tetrasodium pyrophosphate increases the lathering of coconut oil soap as well as that of certain wetting agents such as sulfonates. Rudy et al.[126] and Huber[67] discussed the calcium complexes of sodium hexameta-, tripoly-, tetrapoly- and pyrophosphates and their effect upon the precipitation, solution and dispersion of calcium soaps. These authors found that hexametaphosphate is much more effective than tripolyphosphate. Gilmore et al.[40] described a series of tests washing bundles of laundry in a commercial laundry using

sodium metaphosphate. The use of 20 pounds of metaphosphate in 400 gallons of soap solution gave excellent quality of work and material savings in soap. Phair[111] and Corsaro[24] described the sequestering value of polyphosphates for calcium and magnesium.

Sodium Hexametaphosphate

Sodium hexametaphosphate has been used in the textile industry to a considerable extent. Markuze[92] claimed that it decreased the fat content of silk and the time of washing, and thus resulted in better dyeing conditions. Volz[149] patented the use of sodium hexametaphosphate or polyphosphates for the washing of linen and other materials, and Rozee[125] described the use of sodium tetraphosphate for the prevention of lime-soap precipitation upon wool.

<div align="center">DISHWASHING COMPOUNDS</div>

The washing of dishes, bottles, cooking and eating utensils was formerly done entirely with soap and by hand. With the advent of dishwashing machines for hotels and restaurants the trend at first was toward strongly alkaline dishwashing compounds containing caustic soda, sodium metasilicate, sodium carbonate, etc. It was soon found that the high temperatures and strong alkalinites used resulted in the etching of glasses and metal articles, espcially aluminum. It was also found that soap curd was redeposited in many cases and not only gave a poor appearance but was a health hazard as well since it furnished material upon which bacteria could grow. Moreover, suds in any quantity interfere with the washing action. With the introduction of home dishwashing machines it was necessary to develop detergent compositions specifically designed for this purpose. Hall[49] patented a soapless polyphosphate-silicate mixture and Schwartz and Gilmore[132] described comparative-tests of polyphosphates and various dishwashing formulas. Mann and Ruchhoft[9] studied hexametaphosphate, tetrasodium pyrophosphate and sodium tetraphosphates as sequestering agents to avoid calcium deposition upon utensils. Machils and Michaels[86] recommended tetrasodium pyrophosphate over trisodium phosphate for dishwashing. MacMahon[89] patented a mixture of sodium tripolyphosphate, trisodium phosphate or soda ash, sodium silicate and a surface-active agent as a dishwashing compound. Cosbie[26] recommended a mixture of sodium metasilicate, trisodium phosphate, sodium carbonate and sodium hexametaphosphate mixed with caustic soda for the cleaning and sterilizing of bottles. Harding and Trebler[55] studied the requirements for a detergent specifically for the dairy industry and concluded that the most effective cleansing agent should contain enough polyphosphate to keep calcium and magnesium salts in solution, a synthetic wetting agent,

and adequate alkalinity to dissolve denatured protein. Hall and Schwartz[43] recommended sodium metaphosphate in dishwashing compounds to avoid films of insoluble alkaline earth salts and soaps, and claim an actual reduction in bacterial count by its use.

In addition to those already cited, a number of patents on detergent compositions containing phosphates have been issued to Alsfeld[1], Block and Metziger[13], the Rumford Chemical Company[127], Crites[27], Benckiser and Draisbach[9], Thomas and Oakley[144], Hubbard and McCullough[66], Bolz and Watzel[14], and Snell[140]. MacMahon[87] patented synthetic detergent briquettes especially adapted for washing machines and for milk cans and bottles containing trisodium phosphate, sodium carbonate, and tetrasodium pyrophosphate together with synthetic detergents. In another patent[88] he claimed the same compositions with hexametaphosphate or tetraphosphate. Meites[97] covered the preparation of a new alkali metal phosphate compound produced by heating powdered P_2O_5 with a trialkali metal orthophosphate. McGhie[95] proposed the addition of a small amount of alkali phosphate to sodium alkyl sulfate type detergents to inhibit corrosion; Lind[84] patented a detergent containing polyphosphate together with the alkali metal salts of sulfonated alkane containing 10 to 18 carbon atoms. Pierce[112] discosed a cleaning and sterilizing agent containing trisodium phosphate, tetrasodium pyrophosphate and nitrate. Garverick and Martin[36] described a laundry detergent containing silicate, and absorptive clay, an alkali metal phosphate and a fatty acid oil. Moose[99] patented a sodium hexametaphosphate agglomerate containing soda ash.

For full descriptions of these phosphate detergents the reader is referred to the U. S. Patents listed in Tables 25 and 28 of the Appendix.

MANUFACTURE OF SODIUM PHOSPHATES

Trisodium Phosphate

The manufacture of sodium phosphates is of considerable magnitude. One of the largest tonnage items is crystalline trisodium phosphate. This material is a dry crystalline product which can be handled and shipped easily. The product of commerce has the approximate formula of $Na_3PO_4 \cdot 12H_2O$ but varies from manufacturer to manufacturer by having more or less free alkalinity and somewhat less water than is indicated above.

The manufacture of trisodium phosphate is now conducted on an extensive scale and though the reactions involved are relatively simple, experience and skill are required in order to obtain a product which will satisfactorily meet the specifications required by the trade. Moreover, since this has become a highly competitive business and the producer must work on a rather narrow margin of profit, it is necessary to use the best and

most up-to-date mechanical equipment in order to keep labor and handling charges to a minimum.

Since the third atom of hydrogen in phosphoric acid cannot be replaced by the sodium in soda ash, the chemical reactions involved in the manufacture of trisodium phosphate must be carried out in two stages:

(1) The production of disodium phosphate by the action of phosphoric acid on a solution of soda ash:

$$Na_2CO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + CO_2 + H_2O$$
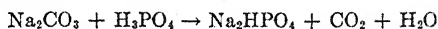
(2) The production of trisodium phosphate by treating the solution of disodium phosphate with sodium hydroxide:

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$
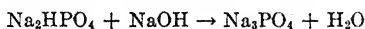
The process is carried out as follows:

The solution of soda ash (along with the mother liquor from a previous batch of trisodium phosphate) is run into large steel-lined tanks fitted with mechanical stirrers and having steam coils to keep the solution at boiling temperature. Sufficient strong phosphoric acid is then added to produce a solution of disodium phosphate which is pumped to a filter press to remove certain precipitated impurities. The cake in the filter press is then washed and the wash water used to help dissolve the next batch of soda ash.

The clear solution of disodium phosphate is then pumped into another mixing vat similar to that used in the first step and a sufficient quantity of a strong solution of caustic soda added to produce a saturated solution of trisodium phosphate. This hot solution is also passed through a filter press and is then either run into crystallizing tanks or though a mechanical crystallizer where it is cooled. During the cooling operation most of the trisodium phosphate drops out in the form of needle-like crystals containing 12 molecules of water of crystallization ($Na_3PO_4 \cdot 12H_2O$).

These crystals are drained and then shoveled into a centrifuge, washed with a small quantity of water to remove the mother liquor and whirled till they contain less than 10 per cent of free moisture. They are then discharged into a hopper, fed to a rotary drier and dried at a temperature insufficient to drive off the water of crystallization.*

The product is then cooled to prevent subsequent caking, discharged into the boot of an elevator and either carried to a storage bin or run over screens to separate the fines from the coarse crystals. The one or more grades of crystals are then packed in barrels, kegs, or sacks for the market.

The mother liquor from the drained crystals as well as that from the wringer goes back into the system in making up new charges. The cycle is repeated until this liquor is too impure for use.

* Since $Na_3PO_4 \cdot 12H_2O$ dissolves in its own water of crystallization at 70°C, great care must be exercised in drying the product.

A flow sheet showing the various steps in the manufacture of trisodium phosphate is given in Figure 1.
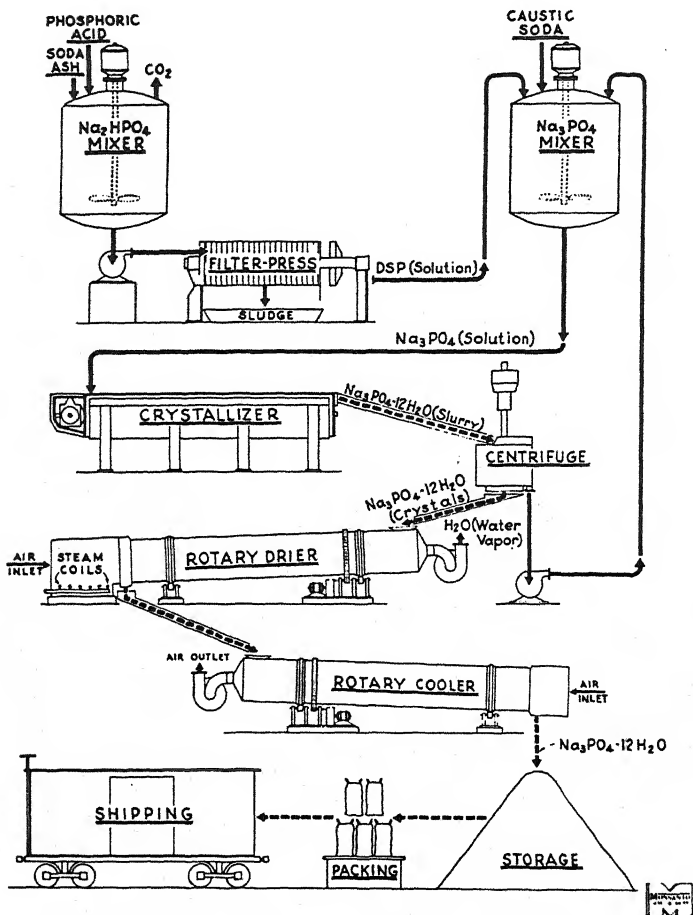
FIGURE 1. Flow sheet for trisodium phosphate.

Tetrasodium Pyrophosphate

The disodium phosphate solution made from phosphoric acid and soda ash may be drum dried to give anhydrous Na_2HPO_4 or crystallized to give $Na_2HPO_4 \cdot 2H_2O$ or $Na_2HPO_4 \cdot 7H_2O$. These various forms of disodium phosphate are then calcined at a high temperature to yield tetrasodium pyrophosphate according to the following equation[25]:

$$2Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$$

$$2Na_2HPO_4 \cdot 2H_2O \rightarrow Na_4P_2O_7 + 3H_2O$$
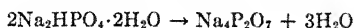
A flow sheet showing the manufacture of tetrasodium pyrophosphate is given in Figure 2.
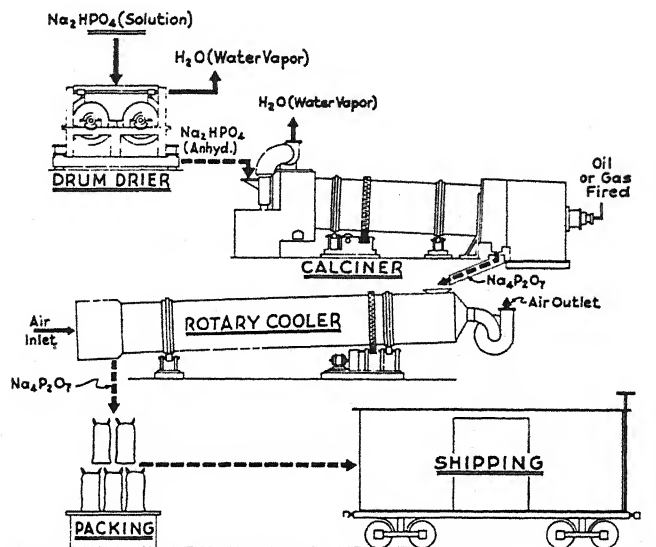
FIGURE 2. Flow sheet for tetrasodium pyrophosphate.

Glassy Sodium Metaphosphate

The process for making glassy sodium metaphosphate is carried out in two steps: (1) making a solution of substantially pure monosodium phosphate (NaH_2PO_4), and (2), fusing this material to form glassy sodium metaphosphate. The product is run out of the furnace in a molten condition and quickly chilled. The equations below indicate the reaction in the two steps[25]:

$$2H_3PO_4 + Na_2CO_3 \rightarrow 2NaH_2PO_4 + CO_2 + H_2O$$

$$nNaH_2PO_4 \rightarrow (NaPO_3)_n + nH_2O$$
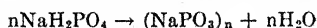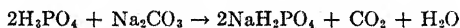
A flow sheet showing the manufacture of glassy sodium metaphosphate is given in Figure 3.

Sodium Polyphosphates

A number of polyphosphates are described in the literature such as sodium hexametaphosphate ($Na_9PO_3)_6$, sodium heptaphosphate ($Na_9P_7O_{22}$),

sodium tripolyphosphate ($Na_5P_3O_{10}$), and sodium tetraphosphate ($Na_6P_4O_{13}$)[24] as well as varieties of these. The structure of these is still in dispute, but Partridge[108] and his co-workers have presented a phase diagram of the system $NaPO_3Na_4P_2O_7$ (Figure 4). This diagram identifies only three molecular compositions in the system, namely, $NaPO_3$, $Na_4P_2O_7$ and $Na_5P_3O_{10}$. Suffice it to say that the chemistry of the polyphosphates is highly complex but they are a series of compounds with very interesting properties. With the doubt as to actual existence of the tetra and hepta
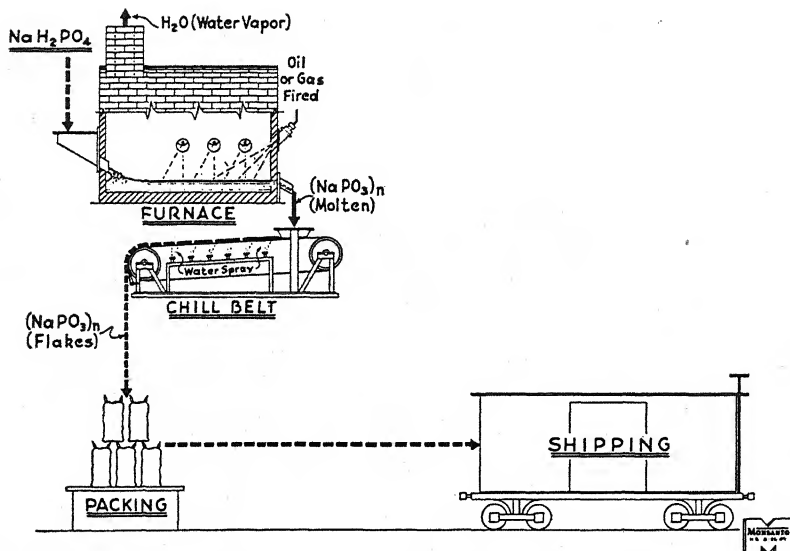
FIGURE 3. Flow sheet for glassy sodium metaphosphate.

phosphates it probably will be well to follow the suggestions of Partridge[108] as to nomenclature. Jackson[70] prepared sodium tripolyphosphate by slowly cooling a melt of 28 parts $NaPO_3$ and 72 parts $Na_4P_4O_7$. Hatch[62] made a tripolyphosphate by dissolving sodium trimetaphosphate in caustic soda. King[78] produced tripolyphosphate by spray-drying a solution containing the proper ratio of Na_2O to P_2O_5 at 550 to 600°C. Wilson[152] proposed a method of manufacturing stabilized polyphosphates by fusion of the proper Na_2O to P_2O_5 ratio with alkali metal salts such as Na_2SO_4. King[76] produced vitreous polyphosphates by quickly chilling the melt. Alsfeld[1] prepared polyphosphates by heating a mixture of primary and secondary orthophosphates, the reactions involved being represented as follows:

$$NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2H_2O \text{ (sodium tripolyphosphate)}$$

$$2NaH_2PO_4 + 2Na_2HPO_4 \rightarrow Na_4P_4O_{12} + 3H_2O \text{ (sodium tetraphosphate)}$$
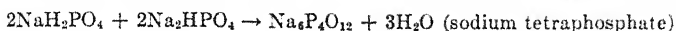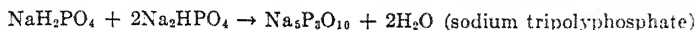
Unquestionably the consumption of alkali metal phosphates and their derivatives for water softeners detergents and soap builders is increasing at a rapid rate. Moreover as the composition of some of these complex compounds are more thoroughly understood and methods of preparing them

Nominal composition, per cent. $Na_4P_2O_7$.
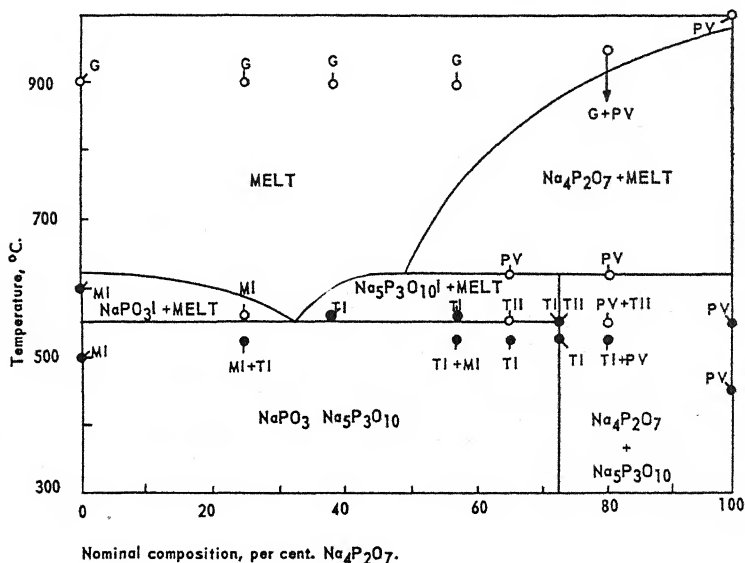
FIGURE 4. The system $NaPO_3$-$Na_4P_2O_7$: open circles represent samples quenched from the indicated temperature; solid circles, samples reheated at the indicated temperature. The identity of the resultant constituents revealed by the X-ray is indicated as follows: G, glass, no crystalline constituent; MI, $NaPO_3$I; TI, $Na_5P_3O_{10}$I; TII, $Na_5P_3O_{10}$II; PV, $Na_4P_2O_7$V.

projected, new and expanded uses will be developed insuring even wider industrial applications.

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25. The Esters of Phosphoric Acid and Their Industrial Applications

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INTRODUCTION

Although the chemical literature is filled with descriptions of organic compounds of phosphorus, only the esters and derivatives of orthophosphoric acid have attained sufficient economic interest at this time to warrant discussion in a book devoted chiefly to phosphate products of commercial importance.

The phosphoric acid esters, which is to say the "organic salts" of this acid, can be thought of as the partial or complete substitution of aliphatic or cyclic organic groups for the hydrogen atoms of phosphoric acid. Thus, proceeding from ortho phosphoric acid, the structural formula of which may be represented thus:

$$\begin{array}{c} HO \\ \diagdown \\ HO\!-\!P\!=\!O \\ \diagup \\ HO \end{array}$$
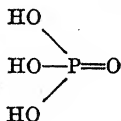
organic groups may be added to yield a mono, di or tri ester as follows:

$$\begin{array}{ccc} RO & RO & RO \\ \diagdown & \diagdown & \diagdown \\ HO\!-\!P\!=\!O & RO\!-\!P\!=\!O & RO\!-\!P\!=\!O \\ \diagup & \diagup & \diagup \\ HO & HO & RO \end{array}$$
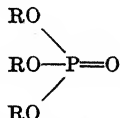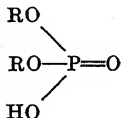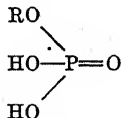
where R represents an aliphatic or cyclic group.

The esterification reaction, however, usually is not carried out with phosphoric acid, but rather with a more active pentavalent compound such as phosphorus oxychloride, phosphorus pentoxide, or phosphorus pentachloride. Industrially all of these intermediates are obtained directly from elemental phosphorus in a high degree of purity. Unfortunately, the production figures for only a few of the more important phosphoric esters are reported statistically, and these compounds are all plasticizers. Since plas-

ticizers represent the greatest part of the consumption of phosphate esters at this time, the figures, though not inclusive, are indicative. Figure 1 shows the phosphate plasticizers produced between 1941 and 1948 as reported by the U. S. Tariff Commission[48].

Prior to 1943 only tricresyl phosphate was reported, and in that year the Acyclic Phosphates were reported as a group. The acyclic phosphates probably include triethyl and tributyl phosphate and possibly others. The figure for 1948 is an estimate as only the tentative figure for tricresyl phosphate was available at the time of writing.
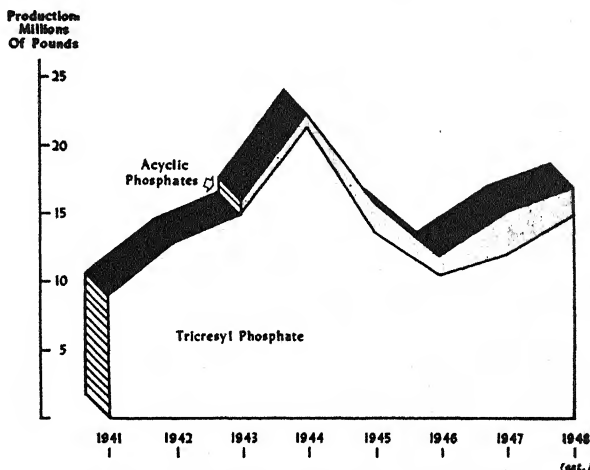
FIGURE 1. Chart of the annual production of the neutral esters of phosphoric acid which are used as plasticizers.

The considerable dip in the production of phosphate esters in Figure 1 was caused in part by the end of the war and the reduction of military demands, and partly by the short supply of raw materials, for example, cresol.

The dollar value of the sales of the phosphate ester plasticizers in 1947 was reported by the Tariff Commission as being almost five million dollars. It can be assumed that if the figures were available for the production and sales of the other phosphoric acid esters and for applications other than as plasticizers, the value of these products would be appreciably above this figure. Even more important than their present worth are the promising signs of growth which the organic phosphates show; their potentialities for the future are quite marked*.

* Recent data show that approximately nine million pounds of phosphorus were used in the manufacture of plasticizers in 1950.

Neutral Esters of Phosphoric Acid

The Trialkyl Phosphates

The trialkyl phosphates, or neutral alkyl esters of ortho phosphoric acid, have been extensively investigated over a number of years, and a considerable variety of applications have been developed. Of the neutral esters triethyl phosphate was first synthesized in 1849, by heating lead diethyl phosphate[105]. Several other reactions by which the trialkyl phosphates have been prepared[13, 54, 61, 102, 103] are illustrated below:

$$Ag_3PO_4 + 3C_2H_5I \rightarrow (C_2H_5)_3PO_4 + 3AgI \tag{1}$$

$$3C_2H_5ONa + POCl_3 \rightarrow (C_2H_5)_3PO_4 + 3NaCl \tag{2}$$

$$3C_2H_5OH + POCl_3 \rightarrow (C_2H_5)_3PO_4 + 3HCl \tag{3}$$

$$3C_2H_5OH + PCl_3 \rightarrow (C_2H_5)_3PO_3 + 3HCl \tag{4}$$

$$(C_2H_5)_3PO_3 + SO_3 \rightarrow (C_2H_5)_3PO_4 + SO_2$$

$$3C_2H_5OC_2H_5 + P_2O_5 \rightarrow 2(C_2H_5)_3PO_4 \tag{5}$$

$$3CH_3OH + PCl_3 \rightarrow (CH_3)_2HPO_3 + CH_3Cl + 2HCl \tag{6}$$

$$(CH_3)_2HPO_3 + Cl_2 \rightarrow (CH_3)_2PO_2Cl + HCl$$

$$(CH_3)_2PO_2Cl + NaOCH_3 \rightarrow (CH_3)_3PO_4 + NaCl$$
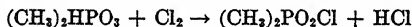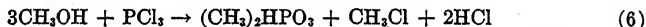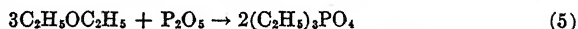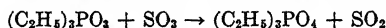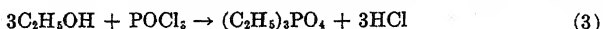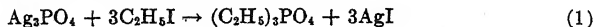
Commercially, one of the most commonly used syntheses is the reaction of an alcohol with phosphorus oxychloride (Equation 3). Difficulty is encountered, however, with the formation of HCl as it forms alkyl chlorides with the alcohol and results in poor yields. A number of methods have been proposed to remove the HCl. These include the use of heat and vacuum, blowing with an inert gas, and neutralization of the HCl with an organic amine or ammonia[25, 33, 52, 60].

Preparation of the trialkyl phosphates is not particularly difficult in the laboratory where economy and yield are not important. However, when large-scale production is attempted numerous problems arise which are not evidenced by the equations above. Chemically, the neutral esters of phosphoric acid are relatively inactive. Some of the esters hydrolyze fairly readily, but otheres require drastic treatment with strong alkali. The phosphate portion of the molecule, of course, cannot be further oxidized and it confers a sometimes surprising resistance to oxidation on the organic portion. The physical characteristics of the homologous esters vary, as might be expected, with the choice of alkyl groups. Whereas the shorter groups give mobile, fairly volatile, water-soluble liquids, the longer chain-length groups give compounds of low solubility and volatility which are more viscous, or are even solids. Table 1 lists some of the neutral esters of phosphoric acid with pertinent physical data[1, 2, 9, 34, 41, 104]. With the ex-

ception of tricetyl phosphate, all the esters listed are liquid at 25°C. The trialkyl phosphates have, in the past, found their greatest use as plasticizers and solvents. Recently, however, appreciable quantities of triethyl phosphate have been used as an intermediate to certain of the organic phosphate insecticides.

The Triaryl Phosphates

Of all of the esters of phosphoric acid, the triaryl phosphates have achieved the greatest industrial importance. This has led to considerable research in methods of synthesis and to the discovery of new applications.

Basically, the triaryl phosphates can be prepared by the same reactions

TABLE 1. PHYSICAL PROPERTIES OF THE TRIALKYL PHOSPHATES

COMPOUND	SP GR AT $(/)°/4°C$	BOILING POINT °C AT MM Hg	SOLUBILITY*			
			Water	Alcohol	Benzene	ChCl₃
Trimethyl phosphate......	1.2144 (20)	62°/5 mm	S	S	S	S
Triethyl phosphate........	1.0695 (20)	75.5°/5 mm	S	S	S	S
Tripropyl phosphate.......	1.0121 (20)	107.5°/5 mm	SS	S	S	S
Triisopropyl phosphate....	0.9867 (20)	83.5°/5 mm	SS	S	S	S
Tributyl phosphate........	0.9766 (20)	138.5°/6 mm	I	S	S	S
Triisobutyl phosphate.....	0.9681 (20)	117°/5.5 mm	I	S	S	S
Triamyl phosphate........	0.9608 (20)	167°/5 mm	I	S	S	S
Trioctyl phosphate........	0.921 (25)	decomp.	I	S	S	S
Tricapryl phosphate.......	0.907 (25)	decomp.	I	S	S	S
Tricetyl phosphate........	—	M.P.: 61°C	I	S	S	S
Tri-(betachloroethyl) phosphate.................	1.4256 (20)	180°/5 mm	I	S	S	S

* S: Soluble; SS: Sparingly soluble; I: Insoluble

as the trialkyl. If anything, the reactions are simpler since the presence of HCl does not give rise to the side reactions of the alkyl syntheses.

Triphenyl phosphate was prepared by Jacobsen in 1875 from phenol and phosphorus oxychloride, a reaction still used commercially today[32]. Some of the syntheses which have been proposed and used for the neutral aryl phosphates[55, 61, 63] are shown below in equations (7), (8), (9), and (10).

$$3C_6H_5OH + POCl_3 \rightarrow (C_6H_5)_3PO_4 + 3HCl \qquad (7)$$

$$3C_6H_5ONa + POCl_3 \rightarrow (C_6H_5)_3PO_4 + 3NaCl \qquad (8)$$

$$3C_6H_5OH + PCl_3 \rightarrow (C_6H_5)_3PO_3 + 3HCl \qquad (9)$$

$$(C_6H_5)_3PO_3 + SO_3 \rightarrow (C_6H_5)_3PO_4 + SO_2$$

$$3C_6H_5OH + PCl_5 + H_2O \rightarrow (C_6H_5)_3PO_4 + 5HCl \qquad (10)$$
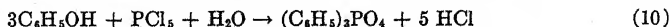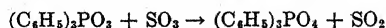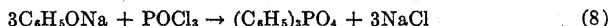
To aid in the synthesis, the removal of the HCl may be effected by blowing or by heat and vacuum[56], and aniline, toluidine, pyridine and other bases have been suggested as catalysts[53].

As are the trialkyl derivatives, the triaryl phosphates are relatively stable chemically. Their physical characteristics vary over rather wide limits though none approach the water solubility or volatility of the lower alkyl derivatives.

The greatest part of the aryl phosphates now produced is used as a plasticizer, and in this application they impart several desirable and unique properties to the plastic composition. These plasticizers will be discussed in detail later in this chapter.

In addition to the neutral esters in which the three organic groups are identical, various combinations of groups can be prepared. Thus, mixed alkyl groups or aryl groups might be used, or both alkyl and aryl groups can be combined. Such combinations greatly increase the variety of characteristics which can be obtained in the phosphate esters. In a sense, phosphate esters can be "tailored" to fit the particular job.

Acid Phosphate Esters

Up to this point, the discussion has been limited to the so-called "neutral" esters or those in which all three of the hydrogen atoms of phosphoric acid have been replaced with an organic group. Obviously, the substitution with organic groups can be stopped at an intermediate point giving compounds in which only one or two of the hydrogen atoms have been replaced. These compounds in which esterification is not complete are the organic acid phosphates, or compounds which retain certain properties of phosphoric acid and have new and different properties conferred by the addition of the organic groups. The mono- and dialkyl esters were prepared and described over one hundred years ago[40], and the mono- and diaryl esters about thirty years later[42]. A number of methods have been used to synthesize these compounds and some of these methods are worth examining. The preparation of *pure* mono- or diesters requires a somewhat expensive synthesis from an industrial point of view as mixtures are usually obtained. The reaction of a trialkyl phosphate with a strong base and subsequent acidification has been used[30]:

$$R_3PO_4 + KOH \rightarrow KR_2PO_4 + ROH \tag{11}$$

$$R_3PO_4 + 2KOH \rightarrow K_2RPO_4 + 2ROH \tag{12}$$
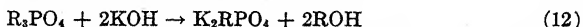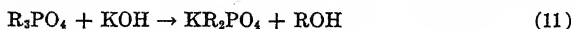
The hydration of an alkyl metaphosphate will give a monoalkyl ester[41]:

$$RPO_3 + HOH \rightarrow H_2RPO_4 \tag{13}$$

and the hydrolysis of a tetra alkyl pyrophosphate will yield the dialkyl ester[38]:

$$R_4P_2O_7 + 2HOH \rightarrow 2HR_2PO_4 \tag{14}$$
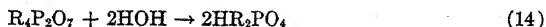
One of the earlier methods of preparation involves the reaction of phosphorus oxychloride, with the appropriate alcohol and subsequent hydrolysis:

$$ROH + POCl_3 \rightarrow RPO_2Cl_2 + HCl \tag{15}$$

$$RPO_2Cl_2 + 2HOH \rightarrow H_2RPO_4 + 2HCl \tag{16}$$

$$2ROH + POCl_3 \rightarrow R_2PO_3Cl + 2HCl \tag{17}$$

$$R_2PO_3Cl + HOH \rightarrow HR_2PO_4 + HCl \tag{18}$$
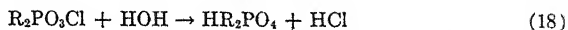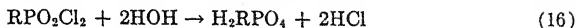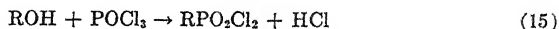
This reaction tends to give all three esters—primary, secondary and tertiary—and yields of any one ester are relatively poor. Probably of greatest industrial interest is the reaction of phosphorus pentoxide with an alcohol or ether to form the mono- or diester[30]:

$$2ROH + P_2O_5 + H_2O \rightarrow 2H_2RPO_4 \tag{19}$$

$$4ROH + P_2O_5 \rightarrow 2R_2HPO_4 + H_2O \tag{20}$$
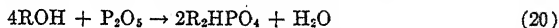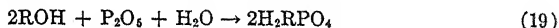
Both the primary and secondary esters form under the conditions of the reaction, and depending on the ratio of alcohol to phosphorus pentoxide and the amount of water present or formed, the amount of diester will vary from 35 to 65 per cent, and the monoester from 65 to 35 per cent[30]. Though the product of this reaction is a mixture, by virtue of its comparatively low cost and, in most applications, the lack of need for a pure ester, it has found considerable use in industry. The mono- and diaryl esters have received less attention in the chemical literature, and probably the chemical industry, than have the alkyl acid esters. Nevertheless these compounds have been found to have a number of applications.

The aryl acid esters have been prepared from the phenol or its salt and phosphorus oxychloride, pentoxide, or pentachloride with later hydrolysis[24, 31, 43]. As in the case of the alkyl derivatives there is a tendency to obtain a mixture of esters in the product.

A considerable difference exists in the physical and chemical properties of the primary and secondary esters as compared to the tertiary or neutral ester. The alkyl acid esters are unstable to heat, many of them decomposing at temperatures well below 200°C[2]. They are strongly acidic and corrosive to certain metals. There is also a tendency toward hydrolysis in water solutions. Table 2 lists some of the properties of the alkyl acid phosphates. It should be noted that the data given are for compounds formed from the reaction of alcohol and phosphorus pentoxide which are probably mixtures. Also, the figures are from two primary sources[2, 3, 30] and may represent mixtures of varying constitution. Nevertheless, the data are indicative of general properties.

In industrial use, the salts of the acid phosphate esters have probably been more important than their parent acids. By neutralizing the organic

acid phosphates with an organic or inorganic base, compounds of considerable usefulness are obtained. Table 3 shows the physical characteristics of some of these alkyl acid salts. As in the previous table the compounds listed are of a commercial grade and the figures should be taken as only indicative[2, 30].

Most of these salts are very soluble in water and are close to neutral in pH. They are more resistant to hydrolysis than the acids and have little corrosive action toward metals. Usually, the salts are supplied as water

TABLE 2. PHYSICAL PROPERTIES OF THE ALKYL ACID PHOSPHATES

COMPOUND	SP GR AT 25°/4°C	DECOMP. POINT—C	SOLUBILITY*			
			Water	Alcohol	Benzene	CHCl₃
R_2HPO_4						
Dimethyl acid phosphate...........	1.34	175	S	S	I	I
Diethyl acid phosphate.............	1.19	>175	S	S	S	PS
Ethyl isoamyl acid phosphate.......	1.07	>175	I	S	S	S
Ethyl octyl acid phosphate.........	1.03	>175	I	S	S	S
Ethyl capryl acid phosphate.......	1.02†	170	I	S	S	S
Dibutyl acid phosphate.............	1.06	>175	I	S	S	S
Butyl amyl acid phosphate	1.04	>175	PS	S	S	S
RH_2PO_4						
Monomethyl acid phosphate........	1.51	170	S	S	I	I
Monoethyl acid phosphate..........	1.43	165	S	S	I	I
Mono isopropyl acid phosphate.....	1.29†	75	S	S	I	I
Monopropyl acid phosphate.........	1.33†	125	S	S	I	I
Monobutyl acid phosphate..........	1.18	105	S	S	S	PS
Mono isoamyl acid phosphate.......	1.14	165	I	S	S	S
Monooctyl acid phosphate..........	1.07	170	I	S	S	S
Monocapryl acid phoshpate........	1.09	105	I	S	S	S

* Solubility: S—Soluble; PS—Partially soluble; I—Insoluble.
† Specific Gravity at 30°/4°C instead of 25°/4°C.

solutions or pastes though, in some cases, an anhydrous product can be prepared.

INDUSTRIAL APPLICATIONS OF PHOSPHORIC ACID ESTERS

Phosphate Esters as Plasticizers

The neutral or tri-esters of phosphoric acid have found their greatest utility as plasticizers. The industrial importance of this field is well defined by the U. S. Tariff Commission's figures on production and sales.

The theory and mechanics of plasticization are involved and complex subjects, and no attempt is made to cover this field in detail. Sufficient background is given, however, on which a critical appraisal of the merits

of the neutral esters as plasticizers can be based. A plasticizer has been defined as a liquid or low-melting solid which is added to a resin to modify

TABLE 3. PHYSICAL PROPERTIES OF THE ALKYL ACID PHOSPHATE SALTS

COMPOUND	CONC. (%)	SP GR AT (/)°/4°C	REFR. INDEX N_D
R_2MPO_4			
Diethyl sodium phosphate.................	78	1.26 (25)	1.41
Ethyl octyl sodium phosphate.............	82	1.12 (30)	1.43
Ethyl octyl potassium phosphate...........	77	1.15 (25)	1.43
Ethyl octyl ammonium phosphate.........	84	1.04 (25)	1.43
Ethyl capryl sodium phosphate............	84	1.07 (75)	1.43
Dibutyl ammonium phosphate.............	88	1.03 (25)	1.43
RM_2PO_4			
Monomethyl ammonium phosphate.........	54	1.25 (30)	1.41
Monomethyl sodium phosphate.............	66	1.53 (30)	
Monomethyl calcium phosphate............	100	2.50 (30)	1.53
Monoethyl ammonium phosphate...........	55	1.24 (30)	1.42
Monoethyl sodium phosphate..............	66	1.47 (30)	1.42
Monoethyl calcium phosphate.............	100	1.92 (30)	1.53
Monoisopropyl ammonium phosphate.......	62	1.20 (30)	1.42
Monoisopropyl sodium phosphate..........	60	1.32 (30)	1.42
Monoisopropyl calcium phosphate.........	100	1.93 (25)	1.48
Monopropyl calcium phosphate............	100	1.77 (25)	1.50
Monobutyl ammonium phosphate..........	60	1.17 (25)	1.43
Monobutyl sodium phosphate..............	71	0.89 (25)	1.43
Monobutyl calcium phosphate.............	100		1.48
Monoisoamyl ammonium phosphate........	77	1.14 (25)	1.43
Monoisoamyl sodium phosphate............	33	1.24 (30)	
Monoisoamyl potassium phosphate.........	66	1.30 (30)	1.43
Monoisoamyl triethanolamine phosphate....	100	1.21 (25)	1.49
R_2MPO_4 and RM_2PO_4, Mixed			
Methyl ammonium phosphate..............	60	1.27 (25)	
Methyl potassium phosphate...............	60	1.48 (25)	
Ethyl triethanolamine phosphate...........	60	1.19 (25)	
Ethyl aminobutyl phosphate...............	60	1.15 (25)	
Ethyl dibutylamine phosphate.............	60	1.04 (25)	
Ethyl sodium potassium phosphate.........	60	1.37 (25)	
Propyl sodium potassium phosphate........	60	1.37 (25)	
Butyl sodium potassium phosphate........	60	1.31 (25)	
Amyl sodium potassium phosphate.........	60	1.35 (25)	

one or more of its physical characteristics. The plasticizer's most important function is to increase the plasticity of the resin so that it can be molded into desired forms[8].

The action of a plasticizer has been compared to that of a solvent, in

that the van der Wall's forces existing between the polymer chains are modified by the plasticizer to substitute polymer-plasticizer bonds for the polymer-polymer bonds[17]. This decrease in the physical bonding forces results, of course, in greater plasticity of the resin.

The physical requirements of a plasticizer are many. First of all it should be a polar type compound. However, it must have low volatility and low water solubility. These latter requirements immediately eliminate most alcohols, acids, amines and low-molecular weight compounds.

Below are listed some of the required and the desirable characteristics of a plasticizer and to what degree the phosphoric esters possess them when properly compounded.

<div align="center">Characteristics of the Phosphate Ester Plasticizers</div>

Required Characteristics	*Suitability of Phosphate Esters*
High polarity	Yes
Compatibility	Excellent*
Plasticizing efficiency	Excellent*
Permanency in resin	Excellent*
Heat stability	Fair to Good
Light stability	Fair to Excellent
Desirable Characteristics	
Flame resistance	Excellent*
Low toxicity	Poor to Good*
Low temperature flexibility	Fair to Excellent*
Resistance to solvents	Good
Electrical properties	Good
Color	Excellent

* Variations in characteristics will be found in different substituent groups and with different resins.

It will be noted that these esters qualify as excellent under the required characteristics of polarity, compatibility, plasticizing efficiency, permanency to ageing and weathering, and light stability. Under desirable characteristics—and these may be required in certain applications—plasticizers containing phosphorus rate high in all categories. Probably the most important of the latter group are the qualities of nonflammability and low toxicity, and esters possessing both of these properties can be made based on phosphorus.

Naturally, the foregoing must be qualified to the extent of choosing the proper substituent groups for the phosphate radical and its use in the proper resin. For example, the flammability of different esters can vary over wide limits: trioctyl phosphate is a relatively flammable plasticizer as compared to tricresyl phosphate which is used where low flammability is required. It is in the choice of the substituent groups that the chemist

and plasticizer expert have their greatest latitude. Although the building of plasticizers is still largely a "cut and try" art, there are certain empirical conclusions which can be applied in the attainment of desired characteristics.

The phosphate radical itself provides certain of the requirements of a good plasticizer: high polarity, permanence, low toxicity, and so on. Coupled with the right alkyl or aryl groups—and it is here that the major
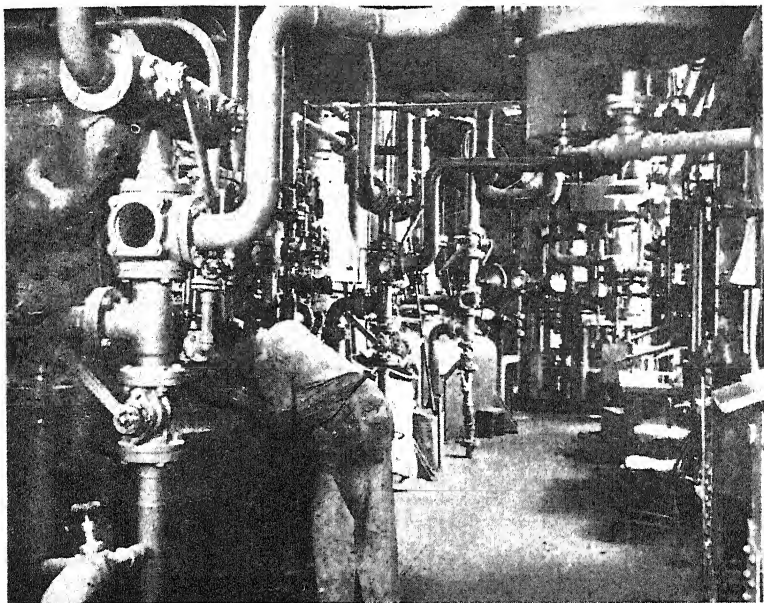
(Courtesy of Monsanto Chemical Co.)

FIGURE 2. The wide use of some of the phosphoric acid esters requires large-scale equipment to provide sufficient production.

problem lies—compounds are formed which are valuable and industrially important plasticizers. About 1920, the first of the phosphate plasticizers reached the industrial stage. These were tricresyl and triphenyl phosphate, for which patents had been issued in 1902, almost twenty years before[50]. Their commercialization was caused by two factors. First, was the necessity of including flame retardants in airplane dopes used during the First World War; second, was control of natural camphor, the standard nitrocellulose plasticizer, by the Japanese monopoly. The high price set by this monopoly gave considerable financial incentive to the development of substitute plasticizers.
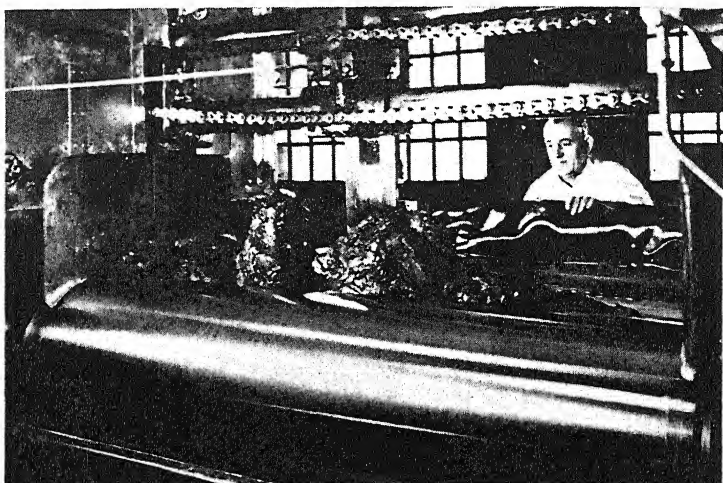
(Courtesy of Monsanto Chemical Co.)

FIGURE 3. Industrial milling of a resin-plasticizer composition prior to its molding into a finished form.
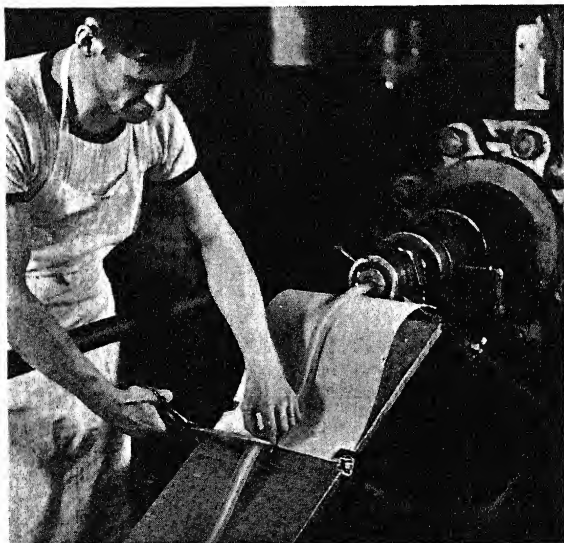
(Courtesy of Monsanto Chemical Co.)

FIGURE 4. Production of seamless tubing by extrusion.

Since 1920 a number of other phosphoric acid esters have entered the plasticizer field. A fairly complete list of these products follows.

Diphenyl cresyl phosphate
Diphenyl 2-ethylhexyl phosphate
Diphenyl o-xenyl phosphate
Di(p-tert.-butyl phenyl) phenyl phosphate
Di(p-tert.-butyl phenyl) 5-tert.-butyl,2-xenyl phosphate
Di(o-xenyl) phenyl phosphate
Tributoxyethyl phosphate

Tributyl phosphate
Tricresyl phosphate
Tridimethylphenyl phosphate
Triethyl phosphate
Tri-2-ethylhexyl phosphate
Triphenyl phosphate
Tri-p-tert.-amylphenyl phosphate
Tri-p-tert.-butylphenyl phosphate

Below are listed a few representative neutral phosphoric acid esters and some of the resins in which they are of value. As may be seen, these esters have a wide range of application and are closely tied with the still rapidly expanding plastics field.

Application of Phosphate Ester Plasticizers

RESIN	TRIPHENYL PHOSPHATE	TRICRESYL PHOSPHATE	DIPHENYL 2-ETHYLHEXYL PHOSPHATE	TRIOCTYL PHOSPHATE
Acrylates	—	—	O	—
Alkyds	—	O	—	—
Cellulose acetate	X	—	O	O
Cellulose nitrate	O	X	O	O
Ethyl cellulose	X	O	O	O
Phenol formaldehyde	—	X	—	—
Polyvinyl acetate	X	O	O	O
Polyvinyl butyral	—	O	O	O
Polyvinyl chloride	O	X	X	X
Polystyrene	—	O	—	—

O = of use; X = of special value.

It is this close relationship of plasticizers to resins that bids fair to establish a permanent market for an effective and competitive plasticizer. If the role of research and development are well discharged, the phosphorus-based esters will remain well within these categories of effectiveness and competitiveness and will find an ever increasing market as our consumption of plastics grows.

The Phosphate Esters as Insecticides

At this time the most important phosphorus-containing insecticides are not, strictly speaking, derivatives of orthophosphoric acid; rather they are polyphosphates and thiophosphates. The relationship is sufficiently close, however, by virtue of synthesis and structure, and the field of sufficient importance that a certain degree of latitude is warranted.

The first published use of the phosphorus esters in the insecticidal field came just after the war when technical experts followed the allied armies into Germany[27, 45]. From their reports it was learned that a considerable amount of research and development had been devoted to the preparation and testing of phosphorus containing compounds against various insect pests.

Whether the insecticides that were discovered were incidental to the search for more potent war gases, or whether the evaluation of animal
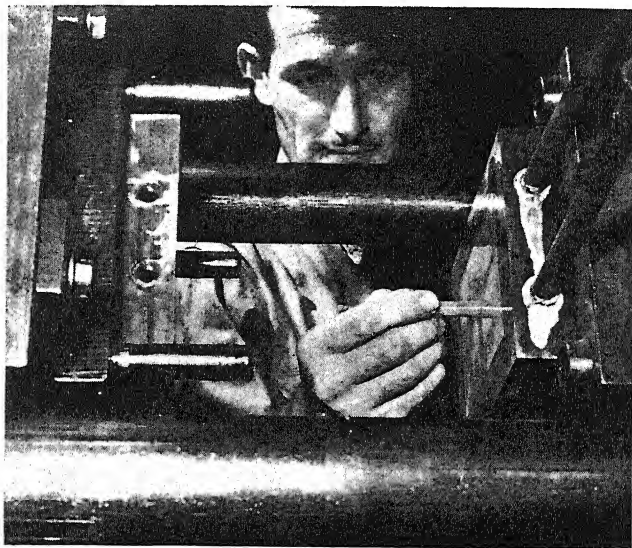
FIGURE 5. Laboratory tests of plasticizer-resin combinations use conditions comparable to actual industrial production.

toxicity of the experimental insecticides gave leads to new gases has not been authoritatively disclosed. In any event the Germans developed very potent insecticides and very poisonous gases based on phosphorus.

A large part of the insecticide development in Germany, at least of the phosphorus-containing compounds, involved the efforts of Gerhard Schrader at the Elberfeld works of I. G. Farben. After the war, Dr. Schrader prepared an account of the preparation and testing of a large number of compounds, including several based on phosphorus[44]. Some of these latter are now being produced in this country. The first of the insecticidally active phosphates found by Schrader was hexaethyl tetraphosphate[26]. The synthesis from triethyl phosphate and phosphorus oxychloride and sup-

posed structure of this product was given as follows:

$$
\begin{aligned}
&\mathrm{O{=}P}\!\!
\begin{array}{l}
\diagup\mathrm{OC_2H_5}\\
\mathrm{-OC_2H_5}\\
\diagdown\mathrm{OC_2H_5}
\end{array}\\[1ex]
&\mathrm{O{=}P}\!\!
\begin{array}{l}
\diagup\mathrm{OC_2H_5}\\
\mathrm{-OC_2H_5}\\
\diagdown\mathrm{OC_2H_5}
\end{array}
\;+\;
\mathrm{Cl}\!-\!\mathrm{P}\!\!
\begin{array}{l}
\mathrm{Cl}\\
\diagdown\\
{=}\mathrm{O}\\
\diagup\\
\mathrm{Cl}
\end{array}
\;\rightarrow\;
\text{(product)}
\;+\;3\,\mathrm{C_2H_5Cl}\\[1ex]
&\mathrm{O{=}P}\!\!
\begin{array}{l}
\diagup\mathrm{OC_2H_5}\\
\mathrm{-OC_2H_5}\\
\diagdown\mathrm{OC_2H_5}
\end{array}
\end{aligned}
\tag{21}
$$
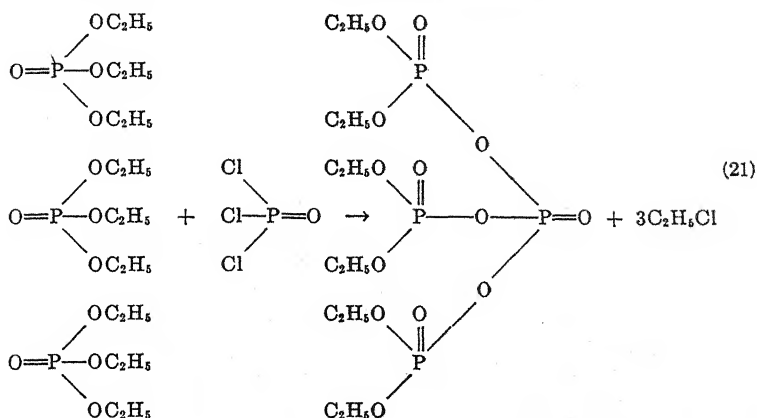
As far as could be observed, the reaction proceeded as indicated with the evolution of three moles of ethyl chloride. When the product was added to water there was an immediate hydrolysis with acid formation, followed by a slow further hydrolysis.

The immediate hydrolysis and the inability to separate any of the constituents made analysis difficult and for some time the product was considered to be hexaethyl tetraphosphate. The final development of a practical analysis changed the picture considerably[20, 28]. It was found that the product called hexaethyl tetraphosphate contained 10 to 15 per cent tetraethyl pyrophosphate, ethyl meta phosphate, possibly some triethyl phosphate and pentaethyl triphosphate, and probably no hexaethyl tetraphosphate at all. Independently, in this country, tetraethyl pyrophosphate was found to be an effective insecticide with a hydrolysis rate comparable to that of so-called hexaethyl tetraphosphate[35]. Classically, the pyrophosphates have been prepared by the reaction of silver pyrophosphate with the appropriate alkyl halide[14] as shown in the reaction (22) below. This is a satisfactory laboratory method but not adaptable to commercial production.

Synthesis of Tetraethyl Pyrophosphate

$$4\mathrm{C_2H_5I} + \mathrm{Ag_4P_2O_7} \rightarrow (\mathrm{C_2H_5})_4\mathrm{P_2O_7} + 4\mathrm{AgI} \tag{22}$$

$$2(\mathrm{C_2H_5O})_2\mathrm{PONa} + \mathrm{Br_2} + \tfrac{1}{2}\mathrm{O_2} \rightarrow (\mathrm{C_2H_5})_4\mathrm{P_2O_7} + 2\mathrm{NaBr} \tag{23}$$

$$(\mathrm{C_2H_5O})_2\mathrm{POCl} + (\mathrm{C_2H_5O})_2\mathrm{PONa} + \tfrac{1}{2}\mathrm{O_2} \rightarrow (\mathrm{C_2H_5})_4\mathrm{P_2O_7} + \mathrm{NaCl} \tag{24}$$

$$(\mathrm{C_2H_5})_4\mathrm{P_2O_5} + \mathrm{O_2} \rightarrow (\mathrm{C_2H_5})_4\mathrm{P_2O_7}$$

$$2(\mathrm{C_2H_5O})_2\mathrm{POCl} + \mathrm{H_2O} \rightarrow (\mathrm{C_2H_5})_4\mathrm{P_2O_7} + 2\mathrm{HCl} \tag{25}$$
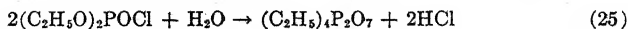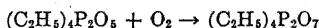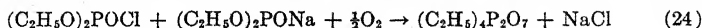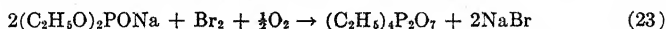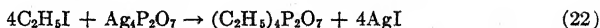
The pyrophosphates have also been prepared from the reaction of sodium diethyl phosphite with chlorine or bromine[5, 6] and from diethyl chloro-phosphite and sodium diethyl phosphite with subsequent oxidation. The most recently published synthesis is the condensation of deithyl phosphoryl chloride in the presence of water[50].

In addition to the above, there are a series of what appear to be similar and analogous reactions that give tetraethyl pyrophosphate along with a mixture of other ethyl phosphates. It will be recalled that triethyl phos-

FIGURE 6. The phosphorus-based insecticides have received widespread acceptance in controlling insect infestations in the green house.

phate can be prepared from diethyl ether and phosphorus pentoxide, and ethyl metaphosphate may also be prepared in the same way. When triethyl phosphate and ethyl metaphosphate are then reacted, tetraethyl pyrophosphate is obtained[7]. It is interesting that, upon heating, tetraethyl pyrophosphate will revert to triethyl phosphate and ethyl metaphosphate.

As noted in the preparation of hexaethyl tetraphosphate, tetraethyl pyrophosphate is formed to the extent of about 10 to 15 per cent. If the ratio of triethyl phosphate to phosphorus oxychloride is increased, the percentage is raised to about 40 per cent. A product identical to hexaethyl tetraphosphate as far as can be told, is formed from the reaction of two

moles of triethyl phosphate with one mole of phosphorus pentoxide[101]. At a ratio of 4 to 1, a product containing about 40 per cent tetraethyl pyrophosphate is formed. In other words the percentage yield in both cases—that is, with both phosphorus oxychloride and phosphorus pentoxide—is similar when one more mole of triethyl phosphate is used with the phosphorus oxychloride than is used with the pentoxide.

This gives rise to the conjecture that perhaps the only function of the extra mole of triethyl phosphate is to react with the oxychloride, splitting off three ethyl chlorides from the one molecule, and leaving phosphorus pentoxide. If this is true then the two reactions are identical as far as the formation of tetraethyl pyrophosphate is concerned.

In any event, both reactions are presumed to be used commercially to prepare a technical product containing about 40 per cent tetraethyl pyrophosphate, and this product is used directly as an insecticide.

Tetraethyl pyrophosphate has been found to be toxic to nearly every insect upon which it has been tested. Commercial control of a large number of insect pests has been accomplished by the use of this compound as a spray solution, emulsion, aerosol and dust. These insects include many species of aphids and mites, scale, plum curculio, pear psylla, leaf hoppers, white fly, mealy bug, and others.

One of the unique characteristics of tetraethyl pyrophosphate is its rapid hydrolysis. It is hygroscopic and will absorb quickly from the air sufficient moisture to completely hydrolyze, the hydrolysis product being diethyl acid phosphate.

The half life, or length of time required to hydrolyze half of the tetraethyl pyrophosphate present, is about seven hours at room temperature[29]. Thus at the end of three days only about one-fifteen-hundredth of the original concentration of tetraethyl pyrophosphate is left.

In those applications where a long lasting residue is wanted, this characteristic hydrolysis is a drawback. However, when toxic residues on food crops are undesirable, the natural detoxification of tetraethyl pyrophosphate is highly advantageous—the end product, diethyl acid phosphate, being to all intents and purposes nontoxic.

The second compound found by Schrader which has reached the commercial stage both here and in Germany is O,O-diethyl-p-nitrophenyl thiophosphate[59]. This chemical has been given the common name parathion, and this appellation will be used in the following[39].

Parathion was synthesized by reacting sulfur with phosphorus trichloride, forming thiophosphoryl chloride. This is then reacted with two moles of sodium ethylate and one mole of sodium paranitrophenate to form parathion. These reactions are illustrated in equations (26), (27), and (28).

Synthesis of Parathion

$$PCl_3 + S \rightarrow PSCl_3 \qquad (26)$$

$$PSCl_3 + 2NaOC_2H_5 \rightarrow (C_2H_5O)_2PSCl + 2NaCl \qquad (27)$$

$$(C_2H_5O)_2PSCl + NaOC_6H_5NO_2 \rightarrow \qquad (28)$$
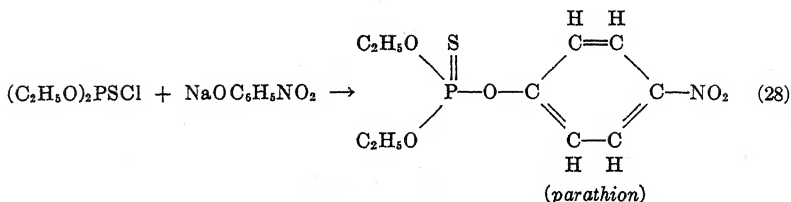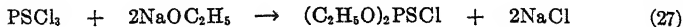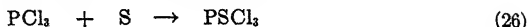
(parathion)

Parathion has been found to be a highly effective insecticide. Its activity is roughly equivalent to that of tetraethyl pyrophosphate, and in addition it is toxic to resting stages and insect eggs as well as possessing residual insecticial properties. Paration has been found effective against mites and aphids appearing on a wide variety of crops, coddling moth, Colorado potato beetle, ants, flies, worms, corn earworms, Japanese beetle grubs, plum curculio, and many other insects.

In some cases tetraethyl pyrophosphate and parathion complement each other in their applicability. In other uses, where both have been found effective, the choice rests on the individual characteristics of the two insecticides.

In addition to the three phosphorus ester insecticides already discussed, one other has been recently announced in this country as being available in experimental quantities. This is tetraethyl dithionopyrophosphate[36]. The structure of this compound is given as:
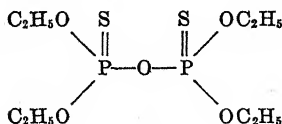
Schrader called this compound Lime-stable Bladan in recognition of the fact that it was more resistant to alkaline hydrolysis than its parent compound, tetraethyl pyrophosphate.

One other class of organic-phosphorus compounds was reported by Schrader and is now under active development in this country and abroad. These compounds are known as systemic insecticides—chemicals which are absorbed by the plant and render the plant itself insecticidal. This is an extremely promising field and may lead to an entirely new approach to the protection of crops against pests of all kinds.

All of the insecticides which have been mentioned are highly toxic not

only to insects but to warm-blooded animals as well. By intravenous injection some of them have LD 50's that fall in the range of 1 to 10 mg/kg of body weight. This varies considerably, however, with the test animal and with the mode of administration. In addition, these phosphate esters have the property of being absorbed readily through the skin which makes careful handling necessary. One of the greatest fields for improvement in the phosphate insecticides is in the reduction of the animal toxicity as compared to the insecticidal activity.

Notwithstanding this disadvantage of animal toxicity, it appears that these new insecticides built around the phosphorus atom have already made a considerable place for themselves, and give every promise of even greater utility.

OTHER USES FOR THE ALKYL PHOSPHATES

Other actual and suggested uses for the trialkyl phosphates are as catalysts in the dehydration of glycols, olefinic alcohols[85], as accelerators in the curing of certain resins[87, 88], as special type lubricating agents[84], as additions to gunpowder[83], and as absorbing fluids in refrigerating systems[64].

The alkyl *acid* phosphates have been used or proposed for the following purposes:

As a flux in the soldering or welding of zinc, magnesium and aluminum, it is claimed that toxic fumes and corrosive residues are thus avoided[42]; as catalysts in the hardening of urea-formaldehyde resins[93], as anticorrosion or passivating agents which may be incorporated in solvents and oils[79, 91, 94], as tanning agents and in the reduction of gelatination of hides [57, 76], as an intensifying agent in vat dyestuffs[3], as addition agents to colloidal systems to alter physical state[3], and as polymerizing agents in unsaturated compounds such as tung oil[78].

Applications of the *salts* of alkyl acid phosphates are quite varied and include the following uses: surface activating agents[62, 68, 77], flameproofing agents[4, 30, 67, 89, 95], as antifreeze liquids[30, 92], as special fertilizers[46, 47, 71, 72, 73, 74, 75], as stabilizers for concentrating latex[65], as a textile preservative[19], and as an ingredient of vat printing pastes[30].

OTHER USES FOR THE ARYL PHOSPHATES

The aryl phosphates (particularly tricresyl phosphate), have achieved an important place in the hydraulic fluid and lubricant field. In both of these applications certain characteristics are either desirable or essential. These include lubricity or oil-like properties, high film strength, resistence to heat and oxidation over a wide range of temperatures, lack of flammability and noncorrosiveness. Their characteristics make the aryl phosphates not only valuable as additives, but as lubricants in their own right[22].

The aryl *acid* phosphates have been suggested in several applications including phosphorylating agents, analytical reagents, and rust and corrosion inhibitors[11, 12, 100].
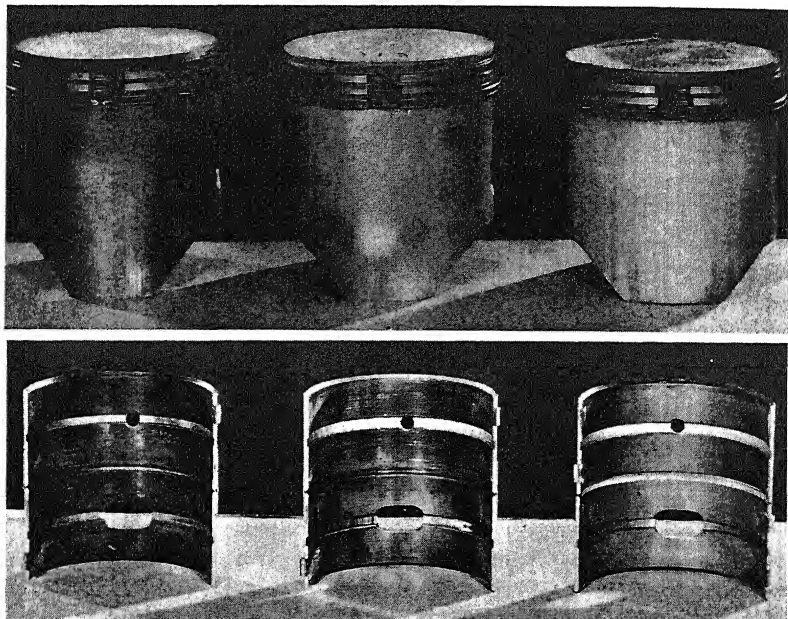
FIGURE 7. The oil used with the piston and bearing on the left, above, contained no additive, that in the center a small percentage, and that on the right a larger percentage of additive. The decrease in carbon and lacquer deposition from left to right can be readily seen.

Though no industrial applications of the *salts* of the aryl acid phosphates have come to the attention of the writer, it seems reasonable to assume that there are or will be such uses.

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26. Phosphating of Metals

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INTRODUCTION

The prevention of corrosion of metal surfaces exposed to abnormal or even ordinary oxidizing conditions is a problem on which much time and careful research have been spent. Most structural iron and steel is protected by paint or pigments fairly impervious to gases and moisture, but these are merely adherent films which are adversely affected by contraction, expansion and abrasive influences.

The importance of having rust-proof coatings which penetrate or molecularly bond themselves to metal surfaces and hence are not subject to deterioration from expansion and contraction was early recognized, and a number of processes based on the formation of oxide, sulfide and metallic films have been tried with more or less success. The plating of iron and steel with tin, zinc, copper, brass, nickel and chromium has been practiced for many years, but the use of such plated metal is restricted either by its rate of deterioration or its cost.

Oxide or anodized coatings on metals (notably aluminum) have been successfully employed, but such coatings are not applicable to iron and steel. Sulfide films are of rather limited value since they have a tendency to oxidize and often are readily removed by mild abrasion.

Through the agency of phosphoric acid, however, processes for the production of highly resistant films for metals have been developed that not only are relatively rust proof in themselves, but act as an excellent base for paint and other protective coatings.

It is estimated that in 1950 sixty million pounds of phosphoric acid (75 per cent) were used for metal-working. The major portion of this amount was used in the phosphate treating of metals—particularly iron, steel, zinc, aluminum, and cadmium—prior to painting in order to improve the adhesion of paint-to-metal surfaces and increase the corrosion resistance of the painted surface. The use of phosphoric acid for this purpose is increasing annually and today nearly all of the painted sheet metal parts of automobiles, refrigerators, washing machines, and other electrical appliances are subjected to one of the commercial phosphate treatments before painting.

A large tonnage of phosphoric acid is used in coating metal with a heavy, absorbent, crystalline phosphate film such as the well known "Parkerized" finish, which provides substantial corrosion resistance without the benefit of paint or organic applications. Such coatings are rendered more effective, by applying thin films of soluble oils, waxes or varnishes and are valuable as corrosion-resistant finishes on iron and steel articles such as nuts, bolts, screws, washers, tools, ordnance parts, etc.

A further, and highly important use of phosphoric acid in the metal industry is that of forming a phosphate coating on machine elements, such as pistons, piston rings, camshafts, tappets, gears, etc. This acts as a wear-resistant coating on the frictional surface of such elements[9]. This coating, when oiled and used as a bearing surface, becomes so smoothly burnished that friction, with the attendant evils of scuffing, scoring, galling, and tearing of the metal, is reduced to a minimum.

Phosphoric acid is also rapidly gaining prominence in the metal industry for the production of phosphate coatings which are useful as drawing[26] and stamping lubricants[30], and for the local nitriding of steel[31].

A complete list of U. S. Patents pertaining to phosphate coatings for metals is given in Table 29 of the Appendix.

Nature of Phosphate Coating Solutions and Coatings

Bascially, the traditional phosphate coating bath is a dilute orthophosphoric acid solution saturated with a primary metal orthophosphate. The metal phosphate is held in solution by virtue of the presence of the free phosphoric acid. While various metal phosphates have been used, commercial experience has shown the phosphates of zinc or manganese to be the most acceptable. When an iron or steel surface is subjected to the action of such a phosphate coating solution, the free phosphoric acid exerts a solvent action on the iron, causing a decrease of free acid at the metal-solution interface, resulting in the precipitation of metal phosphate on the surface of the metal being coated. The metal phosphate deposited on the surface of the metal being coated is a secondary or tertiary metal phosphate, as contrasted with the primary metal phosphate which is present in the coating solution. Typical coating solutions for application by immersion are as follows:

A

Zinc phosphate, $Zn(H_2PO_4)_2$	0.244 lb
Phosphoric acid (75%)	0.007 gal
Water	0.976 gal
	1.000 gal

B

Manganese phosphate, $Mn(H_2PO_4)_2$	0.298 lb
Phosphoric acid (75%)	0.011 gal
Water	0.966 gal
	———
	1.000 gal

The nature of the phosphate coating and the rapidity with which it is formed are governed by several factors: (1) the cleaning and pretreatment of the metallic surface prior to subjecting it to the coating solution; (2) the ratio of the free to combined acid in the solution; (3) the presence in the coating solution of various accelerating agents, such as oxidizing agents and small quantities of metals less basic than iron; (4) the method of application such as brush, immersion, or spray; (5) the temperature of the coating solution.

In physical appearance, phosphate coatings vary from the heavy, dark gray, almost black coarse crystalline coatings produced in the immersion manganese phosphate baths, weighing in the neighborhood of 2,500 mg/sq ft and having a thickness of about 0.0002 inches, to the thinner, smoother coatings produced in the spray zinc phosphate baths, which are light gray in color, having a smooth slate-like texture and appearance, weighing approximately 200 mg/sq ft and about 0.000025 inches thick. The heavier coatings produced by the manganese phosphate baths are of the type used for obtaining corrosion protection on iron and steel surfaces which are not subsequently painted. This type of coating has been found to be most useful as a wear-resistant coating on friction-bearing surfaces. The thinner, smoother coatings resulting from the zinc phosphate type baths are more favored as bases for paint, as the smooth coating produced, while serving as an excellent corrosion-resistant bonding medium for paint, does not interfere with the inherent luster of the latter.

PHOSPHATING PROCESSES

In the past seventy-five years patent literature has suggested many processes using phosphoric acid in treating metal. Of these many processes, only a few have proved to be of outstanding use to the industry. The three most prominent processes are: the "Manganese Phosphate Coating Process," the "Phosphoric Acid-Organic Solvent Cleaning Process" and the "Zinc Phosphate Coating Process." The manganese and zinc processes differ from the "Phosphoric Acid-Organic Solvent Cleaning Process" in that they are effective through the production of visible coatings of measurable thickness, while the "Phosphoric Acid-Organic Solvent Process" is effective through its cleaning and metal-conditioning action without the production of a visible coating.

Other processes which should be mentioned are those in which phosphoric acid is applied to metal surfaces in combination with a paint base[11, 12], or as an oil base for the purpose of increasing the bonding and corrosion resistance of the applied paint or oil[13]; and the relatively recent cold process amphorous phosphate coatings derived from the soluble molecularly dehydrated phosphate glasses of the type of sodium metaphosphate[24a].

A flow sheet showing a typical phosphating process, as well as the specifications for equipment and materials, is given in Figure 1.

PHOSPHATING OF METALS
FLOW SHEET and EQUIPMENT SPECIFICATIONS
for RINSE PROCESS

STAGE	"A" CLEANING			"B" RINSE	1 PHOSPHATING	2 RINSE	3 ACID.RINSE	4 DRYING
SOLUTION	PHOSPHATIC CLEANER	PHOSPHORIC CLEANER	ALKALI	CLEAN WATER	PHOSPHATING SOLUTION	CLEAN WATER	ACIDULATED WATER (pH 2½ ~ 4½)	HEAT
TANK	MILD STEEL	LEAD or RUBBER LINED	MILD STEEL	MILD STEEL	STAINLESS or STAINLESS-CLAD STEEL or KOROSEAL-LINED	MILD STEEL	MILD STEEL	OVEN or INFRA-RED LAMPS
TEMPERATURE	145-160°F	DEPENDS ON GRADE USED	175°F	UNHEATED	110-120°F	UNHEATED	100-120°F	100-150°F
TIME	2 MINS.	4 MINS.	2 MINS.	10-15 SECS. THOROUGH RINSING*	1-2 MINS.	10-15 SECS.	10-15 SECS.	1-2 MINS.
HEAT	STEAM	STEAM IF REQUIRED	STEAM	NONE	STEAM	NONE	STEAM	STEAM or INFRA-RED LAMPS

NOTES: *Spray Rinsing must be used following alkali cleaning. Provision should be made for pumping rinse bath from Stage 2 to Stage B, or an aspirator similar to No. 5296 filter pump of A.H. Thomas, Phila., Pa., can be used. All tanks should be equipped with skimming troughs and bottom drains for cleaning. Crates or racks may be of stainless or mild steel, coated with a plastic facing or coating of Ucilon, furnished by the United Chromium Corp., or equal.

FIGURE 1. Flow sheet and equipment specifications for rinse process.

Manganese Phosphate Coating Process

As early as 1869, Ross[25], a captain in the Royal Regiment of Artillery while on duty in the East Indies, discovered that phosphoric acid applied to a clean surface of iron produced a coating, which would "preserve the iron, steel, or metal so treated from the injurious action (in the shape of rust or other oxide) of water or damp air or perspiration." However, it remained for Coslett in 1907 to discover a practical method for producing phosphate coatings[3]. He prepared what is essentially a ferrous phosphate coating bath by dissolving iron filings in a dilute phosphoric acid solution. This solution produced coatings composed of a mixture of ferrous and ferric phosphates, which were substantially resistant to corrosion. Cos-

lett's disclosures, supplemented by the work of Richards[19] and Allen[1], who suggested the use of manganese phosphate, resulted in the "Parkerizing" process, which was widely accepted by the automobile industry for rust-proofing nuts, bolts, and other small parts.

"Parkerizing" process consisted in placing articles to be coated in a wire basket or tumbling barrel and immersing them in a conventional hot alkaline cleaning bath for removal of grease, oil and dirt. This was followed by a water rinse, after which the articles were pickled in sulfuric acid to remove heavy scale and rust. (In many places sand blasting was used as a very effective substitute for the cleaning and pickling operations.) The pickling operation was followed by a water rinse, after which the articles were immersed in the "Parkerizing" solution.

This solution was made by separate additions of phosphoric acid containing a small amount of dissolved iron and manganese dioxide powder. The directions called for the addition of sufficient acid to the aqueous bath to maintain a definite titration, and for the further additions of a definite quantity of manganese dioxide powder for each gallon of acid that had been required. The resulting coating solution was a mixture of iron and manganese phosphates, which produced a coating composed chiefly of manganese phosphate, along with a substantial percentage of iron phosphate.

The solution was operated at a rolling boil and in order to obtain the desired coating it was necessary to immerse the articles in the bath for about two hours. The coating action was accompanied by a vigorous evolution of hydrogen gas from the surface of the articles being coated, and the cessation of this gassing was an indication that the coating action had been completed. Following the coating bath the articles were rinsed, dried, and immersed in a hot solution of a water-soluble black dye or stain. After removal from the stain and drying, the parts were finally immersed in a paraffin oil to give added protection to the phosphate coated surface.

The modern manganese phosphate coating process is essentially the same as the original process just described, but it is operated in the light of present day knowledge of the workings of phosphate coating solutions. The baths are prepared and replenished with a concentrated manganese phosphate-phosphoric acid solution. Commercial concentrates made by dissolving manganese carbonate and phosphoric acid in water are available. When diluted with the proper quantity of water they produce a coating bath properly balanced with respect to free and combined acid present. In operating the bath the ferrous iron is maintained at a minimum by oxidation with hydrogen peroxide or by aeration. The modern baths are operated at 200 to 210°F and the coating action is completed in 15 to 30 minutes. A view of a manganese phosphate coating installation is shown in Figure 2.

Phosphoric Acid-Organic Solvent Cleaning Process

This process was originally proposed by Feidt[8] in 1914, who claimed a "Method of preparing steel for painting which consists in treating it with an admixture of alcohol and phosphoric acid, which will dissolve oil and act on steel." Feidt's discovery was very timely in that it was made when the automobile industry was beginning to adopt the steel body and was
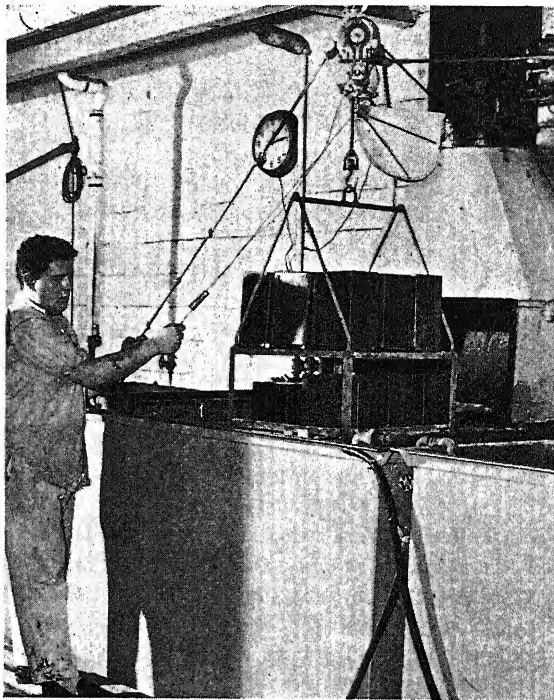
FIGURE 2. Manganese-phosphate installation for coating metal by immersion process.

experiencing tremendous difficulty in obtaining the proper bond between paint and steel, and in preventing blistering and peeling of applied paint coats. The new process proved to be effective in treating metal surfaces prior to painting because it eliminated the causes of blistering and peeling by removing and destroying the corrosive effect of hand marks, grease, soldering acid, light rust, and annealing scale. In addition, the action of phosphoric acid provided a minute etch which promoted the adhesion of paint to metal. The process was found useful in cleaning most metal surfaces.

Many modifications of the Feidt process have been suggested, of which the following are the most useful: that of Gravell[14], who suggested the addition of a thickening agent, such as gelatine; Boyle and Klinger's[17] suggestion of butyl cellosolve as the organic solvent, and Neilson's[18] addition of a wetting agent. Another modification which proved of value was the proposal by Dinley[7] of using a mixture of phosphoric acid, clay, and an organic solvent which was applied to a metal surface, oven dried and removed by brushing.

Several commercial concentrates are available today for carrying out
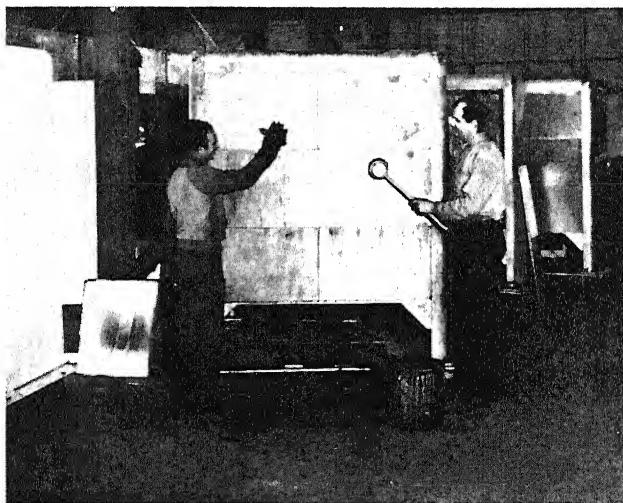
FIGURE 3. Application of organic solvent—phosphoric acid cleaner to commercial refrigerator bodies.

the Phosphoric Acid-Organic Solvent Process. These concentrates contain in the neighborhood of 70 to 75 per cent phosphoric acid and are diluted with 2 to 3 parts of water prior to using. In carrying out the process the metal surface to be cleaned is scrubbed with a long-handled brush with the diluted solution. After the rust and grease are removed, and before the solution dries, the surface is thoroughly rinsed with fresh water. This operation is followed by oven-drying or blowing dry with compressed air. For best results the cleaned and treated surface is painted immediately A modification of this process is known as "The Wipe-Off" process and this varies from that described in that the solution used is of a lower phosphoric acid concentration, which permits removal of the solution by wiping with damp cloths, thus eliminating the conventional fresh water rinsing operation. This process is illustrated in Figure 3.

Zinc Phosphate Coating Process

Zinc phosphate as a metal coating phosphate was originally proposed in 1911 by Coslett[4]. However, because of the difficulties encountered in practical operation of zinc phosphate solutions, many years elapsed and much knowledge of the workings of phosphate solutions was gained before the solution was put into commercial use. Today, a zinc phosphate coating produced from a zinc phosphate coating bath is considered by industry to be the most satisfactory coating for steel and zinc surfaces which are to be painted. The first commercial acceptance of zinc phosphate coating resulted from a process disclosed by Gravell[15]. This process used a solution of phosphoric acid containing some nitric acid and an organic solvent which, when brushed on a galvanized iron surface and allowed to dry, formed a zinc phosphate coating that was effective in bonding paint to the galvanized surface.

In working with the Coslett bath, experimenters found that it exhibited some of the same disturbing characteristics that had been encountered with the manganese phosphate coating baths. The bath initially had a coating speed in the neighborhood of 10 to 15 minutes when operated at a temperature of approximately 180°F, but the time required to complete the coating increased as a succession of metal pieces was processed in the bath. Further, when the bath was allowed to cool and then brought back to operating temperature, the coating characteristics usually changed, so that neither the appearance, the texture of the coating, nor the length of time required for producing it were the same. In order to make the process suitable for industrial use, it was necessary to solve these two problems and find some way of accelerating the initial coating action of the bath.

ACCELERATORS

The accelerators which have been found to be useful in phosphate coating baths may be divided into two classes: (1) the metal-ion type, such as copper or nickel; (2) the oxidizing-agent type, such as a nitrate or hydrogen peroxide. The first disclosure of the metal-ion type of accelerating agent was made in 1919 by Chadwick and Resek[2], who claimed that metals less basic than iron, when present in a phosphate coating solution, would act as accelerators in producing the coating action. Of the various metal ions claimed by Chadwick and Resek, copper proved to be the most valuable and the presence of from 0.002 to 0.04 per cent copper in the phosphate coating solution served to cut the coating time by as much as 50 per cent.

A theory advanced to explain the accelerating action of copper. is that the copper, being less basic than the iron or zinc surface being coated, plates out in minute specks on the surface of the metal, thus setting up a multitude of electrolytic cells, in each of which the basic metal surround-

ing the copper speck dissolves at an accelerated rate and reacts with the coating solution to bring about a more rapid deposition of the phosphate coating.

Another type of metal-ion accelerator which was found useful in producing phosphate coating on zinc was disclosed by Romig[20], who found that the addition of cobalt or nickel to a phosphate coating bath increased the speed of its action, especially on the spangled surface of galvanized iron.

The oxidizing-agent type of accelerating agent was discovered by Tanner and Lodeesen[28], who claimed a method of expediting the coating effect of a metal phosphate solution by using an oxidizing agent in the solution having an oxidation potential not greater than the potential of the common bromates in a dilute phosphate solution. This discovery proved to be of real value to the phosphate coating industry, since it was found that a coating solution containing as little as 0.5 grams of sodium nitrate per 100 cc would produce a coating in 1 to 5 minutes, depending upon the operating temperature and other characteristics of the phosphate bath.

Another oxidizing agent which has proved useful to industry is hydrogen peroxide. This has an oxidation potential considerably higher than the common bromates in a dilute phosphate solution, but was found by Romig[21] to be effective in coating baths where the acidity was maintained below the equilibrium acidity by the continuous addition of a neutralizing agent for phosphoric acid. The neutralizing agent was usually caustic soda.

Another means of accelerating phosphate coating solutions which should be mentioned, since it introduced the zinc phosphate coating solution to industry, is the alternating current process suggested by Romig[22]. This was an electroplating process which used the zinc phosphate or Coslett solution as an electrolyte. In carrying out the process the zinc phosphate coating was electro-deposited on steel by immersing the steel in the electrolyte and passing an alternating current through the steel piece being coated, which served as one electrode and a steel tank which served as the other electrode and which contained the electrolyte. By this means a phosphate coating could be produced in the Coslett solution in from 1 to 3 minutes.

As mentioned previously, one of the most troublesome difficulties with phosphate coating baths was their tendency to get out of balance, i.e., not coat properly if the temperature fluctuated to any great extent. This problem was solved by Thompson and Tanner[29], who found that a bath, in order to be in balance, must have a definite proportion of total acid in solution to free acid, as determined by titration. They showed that the speed of coating could be increased by partially neutralizing the free acid, and that the most effective ratio was between 1 of free acid to 6 of total acidity and 1 of free acid to 15 total acidity. This disclosure proved to be

very valuable as it gave workers with phosphate solutions a means of predetermining the optimum free to total acid proportion of any particular coating solution and of maintaining that range throughout the coating life of the solution.

This technique of operating a coating bath, however, did not yield the answer as to why a freshly prepared bath had a higher coating speed than a bath which had been used to process a succession of metal pieces, even though the used bath were brought back to its original state of balance. The answer to this was given by Romig[23], who found that the slowing up action was due to an accumulation of ferrous iron in the solution. The net effect of accumulated ferrous iron was to change the original zinc or manganese phosphate solution into a zinc-iron or manganese-iron solution, which did not work as rapidly as the original pure solution. Experiments showed that a pure zinc phosphate solution would work faster than a manganese phosphate solution, which in turn would work faster than an all-iron phosphate solution. In other words, contaminating the zinc or the manganese solutions with iron resulted in slowing up their coating action.

This problem was solved by maintaining in the coating bath, at all times, a small quantity of an oxidizing agent capable of oxidizing ferrous iron to ferric iron in a dilute phosphate solution. Ferric phosphate is insoluble in this type of bath and consequently is precipitated out of the solution in the form of a sludge. Sodium nitrate was found to be the most valuable agent for keeping the bath free of ferrous iron. This served a dual function in that it oxidized the ferrous iron to ferric iron, and at the same time, by virtue of the presence of the sodium ion, neutralized the free phosphoric acid that was liberated during the oxidation.

The high-speed phosphate coating solution used today is a zinc phosphate solution containing sodium nitrate as an accelerating agent and sodium nitrite to prevent the accumulation of ferrous iron; this is kept in proper balance by the addition of caustic soda when required. This solution is useful for producing a phosphate coating on both steel and zinc and is applied by either the dip method or by means of a spray.

DIP APPLICATION

In the dip method the parts treated are immersed in six different solutions and are carried through these various solutions mechanically by means of a conveyor. The first stage of the process consists of immersing the parts being treated in a mild alkaline cleaning solution for approximately 5 minutes to remove oil, grease, and other extraneous matter. This is followed by two water rinsing stages. Where an especially smooth phosphate coating is desired the water in the second rinsing stage is replaced with a dilute oxalic acid[24] solution, if steel is being treated, or with a

dilute alkaline phosphate solution[16] if zinc is being treated. After the parts being treated have been cleaned and rinsed they are immersed in the phosphate coating solution, where they remain for 1 to 3 minutes. This solution is maintained at an operating temperature of 180°F. On removal from the phosphate solution the parts are rinsed with hot water, followed by another rinse in a dilute chromic acid solution[5], after which the parts are dried in an oven and are ready for painting (Figure 4).
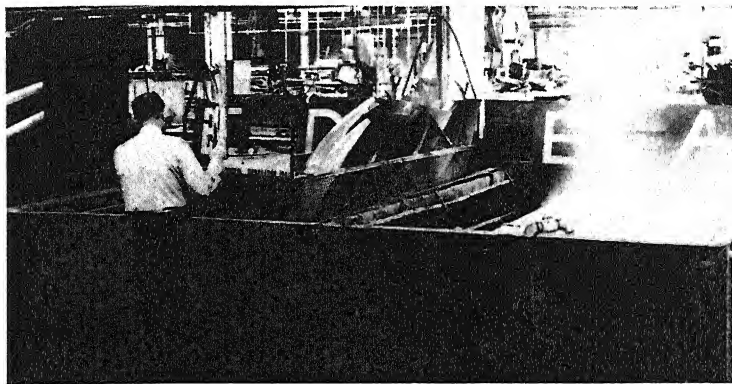
FIGURE 4. Applying phosphate-chromate coating by the Dip Process.

SPRAY APPLICATION

The most efficient and most economical method of applying phosphate coating solutions is by means of a spray. This method is used by the automobile, refrigerator, and washing machine industries in producing phosphate coatings on sheet-metal parts prior to painting. The process is carried out in a six-stage spray washing machine. The parts being treated are carried through the washing machine on an overhead conveyor (in the case of automobile bodies on a floor conveyor), the speed of the conveyor being adjusted so that approximately one minute is required for the parts to pass each of the six-spray stages. Each stage is complete with its own solution tank, pump, risers, nozzles, and draining section. The first stage is the cleaning stage, where the parts being treated are sprayed with an emulsion-type alkali cleaning solution[6] at a temperature of 130 to 140°F. This is followed by two stages of water rinsing. The fourth stage is the zinc phosphate solution and is usually operated at a temperature of 160 to 180°F. This is followed by a water-rinsing stage which in turn is followed by a dilute chromic acid rinsing treatment. On leaving the washing machine the parts go through a drying oven, after which they are ready to be painted (Figure 5).

Cold Phosphating

A useful modification of the immersion and spray zinc phosphate processes just described is known as the room temperature, or cold zinc phosphate process. In this process[27] the cleaning and rinsing solutions are operated at the temperatures specified above but the phosphate coating solution is operated at room temperature or slightly higher. Such low temperature operation is made possible by proportioning the free phosphoric acid in the coating solution so that the solution is about 20 per cent supersaturated with respect to the zinc phosphate present. This solu-
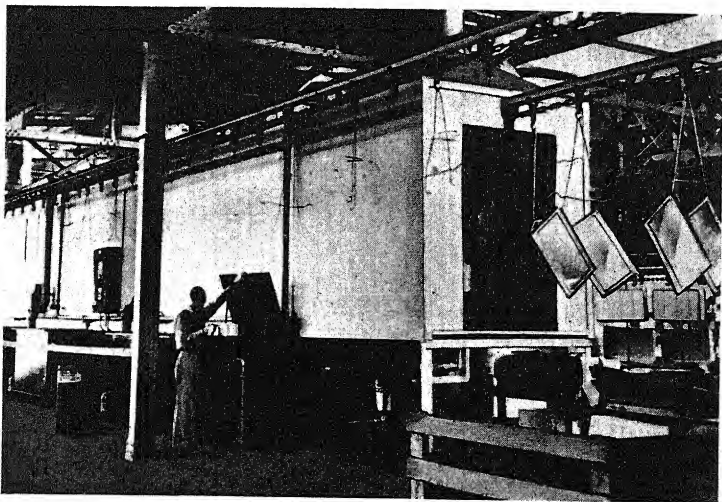
Figure 5. Power spray washer for the application of phosphate coatings to aluminum parts.

tion, with the addition of an oxidizing agent such as sodium nitrite or sodium bromate, will produce a satisfactory coating on a steel surface in from 1 to 2 minutes at temperatures varying from 70 to 120°F, depending upon the extent of the supersaturation of the solution.

Phosphate Coating of Aluminum

A recent development in the phosphate coating industry is a process disclosed by Spruance[27] for producing a phosphate coating on aluminum by subjecting it to a solution containing phosphoric acid, chromic acid, and fluoride ion. The coating produced by this process improves the corrosion resistance of aluminum and serves as a paint-bonding coating. Another phosphate process for aluminum is described by Gibson and

Russell[10]. In this process an aluminum surface is reacted in a metal acid-phosphate solution containing oxidizing agents and a complex fluoride accelerator to produce a crystalline non-metallic phosphate coating adapted to inhibit corrosion and increase the adherence of any applied paint film.

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27. Phosphates in the Manufacture and Refining of Cane Sugar

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PHOSPHORIC ACID IN THE CANE SUGAR INDUSTRY

Phosphoric acid, soluble phosphates, and insoluble phosphates are widely used both in the manufacture and in the refining of cane sugar. Lime is universally used in all sugar work to neutralize organic acids and to form a precipitate that may be removed by filtration or sedimentation, but phosphate in some form is the commonest adjunct to lime in raw cane sugar manufacture and refining.

Early History

Early publications to phosphatic materials as defecants and clarificants appeared over 100 years ago, from 1830 to 1850[79]. This was the period during which the cane sugar industry was being revolutionized.

In raw sugar manufacture, the addition of P_2O_5 in some form was practiced in various processes during the last half of the nineteenth century. Monocalcium phosphate pastes, liquid phosphoric acid, and acid mixed with kieselguhr were the commoner forms in which phosphates were employed. One of the uses of phosphoric acid reported in the latter part of the century was the addition of a small amount of clear acid to the wash water at the centrifugals to brighten the crystals. The more general use of phosphates to improve defecation in raw sugar manufacture is a development of the past 25 years.

In sugar refining, phosphoric acid defecation has gone through three phases. As early as 1850, patents were recorded in England for phosphate-lime defecation, but the use of bullock's blood and lime for clarifying the raw liquor preliminary to char filtration continued for 30 years or more.

On heating the sugar liquor, the albumin in the blood coagulated and trapped the precipitated lime salts, finely suspended matter, waxes, gums, and pectins in a form that could be removed by skimming, or filtration. About 1880, at which time large-scale refining began to develop, the use of blood was almost entirely superseded by the more sanitary and efficient phosphate-lime defecation. Inert filter-aids largely replaced the phosphate-lime treatment about 1915, but within the past 20 years interest has greatly increased in the use of P_2O_5 in refining.

Modern Raw Sugar Clarification

Extensive investigations into the nature of the clarification process in manufacturing raw sugars were begun about 25 years ago by various agencies. For nearly 300 years the universal practice had been to add lime to the cane juice as it came from the mills, heat to the boiling point or above, and then allow the treated juice to stand in open clarifiers until the precipitate settled or floated. After this treatment the clear juice was drawn off and the muds and scums filter-pressed. See the flow sheet (Figure 1 for the manufacture of raw sugar). The procedure was effective for juices from the so-called native canes in various countries, but with the introduction of new varieties of cane and continuous defecation systems it became evident that little or nothing was known scientifically as to what happens to cane juice when subjected to the action of lime and heat.

The Role of Phosphates in Clarification

The accumulation of evidence in the many investigations indicated that the phosphate content of the juice was of the utmost importance in clarification; in fact, for several years it was believed that the amount of P_2O_5 in the juice was a direct measure of the efficiency of the heat and lime process. More recent studies have modified this opinion somewhat, and it is now known that the availability of the phosphate and possibly other factors are also of great importance.

Walker[82], in one of the earlier investigations, showed that phosphate fertilizers added to soils on which cane is grown increased the P_2O_5 in the juice and improved the clarification. McAllep and Bomonti[58] found that Hawaiian juices would not clarify properly unless 30 to 35 parts of P_2O_5 per 100,000 parts of juice were present. Most other investigators during that period, and even later, agreed that for good clarification juice should contain at least 30 parts P_2O_5 per 100,000[41, 42, 65, 15, 33, 20]. In an extensive study in Puerto Rico on "The Influence of Phosphates on Defecation" (or clarification) Paine, Keane, and McCalip[65] proved that it is immaterial whether the phosphate is naturally present or added to the juice as a defecant.

Honig, working with juices from Java[39], said that the P_2O_5 content is the most important constituent of the juice affecting clarification. Norman Smith[75] described the P_2O_5 content as the vital factor in the clarification of juices from Queensland, Australia. The addition of soluble phosphates to juices has become general in the last 20 years. Exceptions to the rule that the more phosphate the better the clarification began to be reported even while others were affirming the principle[19, 47, 59, 67, 70].

Working with canes in the British West Indies, Davies showed that juice from POJ cane (Java variety) averaged 0.035 per cent P_2O_5 and invariably clarified poorly, whereas the juice from another cane variety
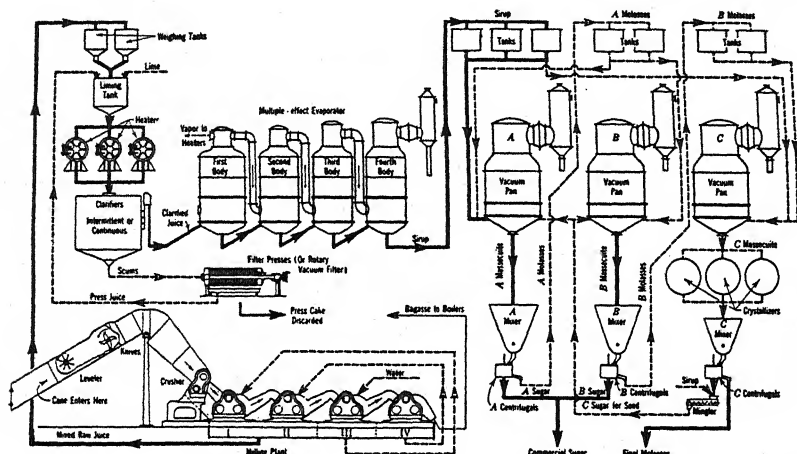
FIGURE 1. Flow sheet for manufacture of raw sugar[76].

containing only 0.013 per cent P_2O_5 was very easily clarified. He also noted after clarification that with the POJ juice the P_2O_5 content was more than twice that of the other.

Summarizing the findings of these various investigators it may be said: (1) that the phosphate content of the cane juice has great bearing on clarification; (2) that it is not an invariable measure as was believed some years ago; and (3) that the addition of a soluble phosphate to the juice is generally beneficial.

Addition of Phosphate to Aid Clarification

On the basis of the above findings it has become general practice in raw sugar manufacture to add a soluble phosphate to the juice, particularly where clarification is difficult[62, 48, 9]. One large sugar factory in Cuba started experimentation with added phosphate in 1928 and the value was

so evident that the procedure is now routine. The material used is powdered triple superphosphate of the type used as a fertilizer and contains 48 per cent P_2O_5. No mechanical equipment is used for the addition. The powdered superphosphate is mixed in small cast iron tanks and the proper amount of the mixture added to each scale tank of juice by the operators to give 44/100 pounds of dry powder per ton of cane. This proportion is equivalent to about 10 parts of P_2O_5 per 100,000 parts of juice. The untreated juice at this factory averages 18 to 20 parts of P_2O_5 per 100,000 parts of juice so that the total P_2O_5 in the juice after treatment approaches 30 parts per 100,000.

The treatment not only improved clarification but greatly improved the quality of the raw sugar. The sugars from phosphated juices are brighter in appearance and of greatly improved refining quality. Because of the wide variation in the character of the cane entering a raw sugar mill, it has not been possible to measure these improvements quantitatively, but the increased elimination of colloids by the addition of phosphate has undoubtedly resulted in an increased yield sufficient to pay for the phosphatation.

Another Cuban factory adds superphosphate in two doses—one to the cold juice and the second to the hot juice before settling. The second application is made with such varieties of cane as POJ 2878, the total added phosphate sometimes reaching 2 pounds per ton of cane ground (about 24 parts per 100,000 of juice). This treatment has produced much clearer juice and sugars of better refining quality.

Direct Consumption Sugars

A sugar boiled directly from concentrated cane juice without the intervening step of making a raw sugar for refining is termed a direct consumption sugar. It is sold under various trade names such as "Plantation Granulated," "Yellow Clarified," and "Turbidnado," depending on the whiteness of the product[77].

Sulfur dioxide and carbon dioxide in combination with lime are customarily used, the processes being called sulfitation and carbonatation, respectively. With sulfitation the general process is to pump the raw juice through a sulfur tower in a countercurrent of sulfur dioxide gas. The juice is then neutralized with lime and the calcium sulfite precipitate filtered by any one of the usual means. The use of phosphoric acid in conjunction with sulfitation gives a sugar of better quality than sulfiting alone and has been used in both South Africa[49] and in Mauritius[37]. According to Dymond[30] phospho-sulfitation as practiced in South Africa showed a much higher removal of gums (alcohol precipitate) than did sulfitation.

PHOSPHATES IN SUGAR REFINING

The first step in the refining of raw cane sugar (Figure 2) is the affination or washing process, by which the film of molasses is removed from the raw sugar crystal. This is carried out by mingling the raw sugar with a heavy sirup, purging the resulting magma in centrifugal machines, and then spraying the retained crystals with a measured quantity of hot water. This washed sugar is then dissolved or melted in hot sweet water in the proportion of two-thirds solids to one-third water.

FIGURE 2. Flow sheet of a refining process. WSL = Washed Sugar Liquor; RSL = Remelt Sugar Liquor.

The raw washed sugar liquor from the melter is generally acid and contains some insolubles, such as bagacillo (fine cane fiber), clay and sand; also fine suspensions and dispersoids, as well as gums, pectins, albumin and other true colloids that have escaped the clarification system in the raw house or that have been formed in the subsequent manufacturing steps. The affination sirup purged from the raw crystals contains the major portion of the impurities from the raw sugar, in similar form but more concentrated. In discussing the use of phosphate for refining, the washed sugar liquor only will be considered.

The purpose of defecation in the refinery is: (1) to remove all insolubles and fine suspended matter to give a clear solution that will char-filter readily, and (2) to remove insofar as possible colloids, gums, pectins,

albumin, and coloring matter. Two processes of a distinctive nature are in use in the United States.

Pressure Filtration with Inert Filter Aids

The widely used pressure filtration was introduced about 1915 when leaf-type pressure filters such as the Sweetland, Kelly and Vallez were brought into commercial use. This process superseded phosphate-lime defecation with bag-filters. Essentially, it consists of neutralizing the acidity of the liquor with milk of lime (7.0 to 7.2 pH) and then adding diatomaceous earth in the amount of 4 to 8 pounds per ton of solids. Filtration is effected at 180°F on either cloth or fine wire-mesh screen in leaf filters. The lime, about 300 pounds per million of solids, together with the heat, precipitates some of the organic and inorganic acids and acid salts and flocculates some of the colloids. The porous mineral filter-aid coats the fabric of the filter, trapping the precipitate and suspended material. The action of the filter-aid is largely mechanical. Although some colloids are adsorbed, there is little color removal[31]. Affination sirups are similarly filtered, using about 40 to 50 pounds of diatomaceous earth per ton of solids. Customarily, the filter-aid from the washed sugar liquor is re-used by beating the cake to slurry with water and then adding this to the lower grade sirup to be filtered, precoating the filter with fresh earth.

Phosphate-Lime Defecation

The use of phosphoric acid and soluble phosphates in early refining has been broadly reviewed. Until the introduction of inert filter-aids, as described in the preceding paragraph, phosphate-lime defecation was the only method in general use, the precipitate being removed by the Taylor bag-filter. This phosphate-lime defecation is still essential in the refineries that employ the Williamson defecation system and is the second method used in the United States. The use of phosphate has been on the increase during the past 20 years, although pressure filtration with diatomaceous earth still predominates[62]. The phosphate defecation is carried out by the basic procedure developed 50 years ago.

The amount of P_2O_5 varies from 0.02 to 0.04 per cent of solids and may be in the form of monocalcium phosphate, phosphoric acid paste, or clear phosphoric acid. The early practice was to make a paste by treating bone char dust with hydrochloric or sulfuric acid. These methods are now of only historical interest.

The present practice is to purchase phosphoric acid in bulk in rubber-lined tank cars. This acid is used either directly or as a paste made by mixing the acid with discard bone char dust. The monocalcium phosphate paste so formed is free of the objectionable qualities of the older hydro-

chloric and sulfuric pastes, as all the salts formed are phosphates. The lime in refineries is the hydrated type, or more recently pulverized quicklime, made into a milk and circulated to the blow-ups and other parts of the plant. The amount of lime used with the phosphate treatment is greater than for the inert filter-aid process because the added P_2O_5 as well as the organic acids of the raw liquor must be neutralized. With ordinary raw sugars about 800 pounds of lime (CaO) per million pounds of melt is average.

The action of the phosphate-lime treatment with heat causes coagulation and precipitation of the greater part of the gums, albumins, and pectins together with the formation of a tricalcium phosphate. The heavy flocculent precipitate entrains with it bagasse fiber, jute, clay, and other insolubles, the finely suspended materials and suspensoids, as well as a large part of the colloids. Long experience and extensive experiments have shown that a large amount of color is removed by the phosphate treatment. This color removal and the elimination of colloids by the acid-lime treatment are its great advantage over pressure filtration with inert filter-aids.

The amount of color removed by phosphoric acid varies from 20 to 40 per cent of the total color, which means that the bone char required for decolorizing will be from 40 to 60 per cent less than with the untreated liquors. Cummins and Morris[18] found that affination sirup treated with 0.1 per cent P_2O_5 showed 20 per cent less color at 495 mμ and 28 per cent less at 620 mμ than did the same sirup pressure-filtered with inert filter-aid neutralized to the same pH (7.2). These investigators stated "the same amount of char will decolorize 50 per cent more sirup treated with 0.1 per cent P_2O_5 than it will untreated."

The clarity of the phosphate-treated sirups in the Cummins-Morris experiments was also much superior to that of the untreated; in fact, the turbidity of the phosphate-treated sirup before char filtration was less than half that of the untreated sirup after char filtration. This clarity due to phosphate treatments is of the utmost importance, as it is a well recognized fact in sugar refining that clear liquors yield much better refined sugars than do cloudy liquors of lighter color.

Williamson Defecation System

The present method of removing the phosphate precipitate from the washed sugar liquor is by air flotation. This system, invented by George B. Williamson[84] of Louisiana in 1918, consists of impregnating the phosphate-treated liquors with air, by any of several means, at a temperature of about 140°F and then heating the liquor in a continuous clarifier so that the air bubbles carry the precipitate to the surface to form a blanket of mud.

The original Williamson clarifier was a flat tank 12 feet long by 6 feet

wide and 1 foot deep, heated by transverse steam pipes. Air-impregnated liquor enters the rear of the clarifier and flows through it at the rate of about 1,000 gallons per hour. The air bubbles rise, because of temperature gradient, carrying with them particles of floc to form a thick blanket of mud covering the entire surface of the liquor. Clear liquor is drawn off the front end through overflow tubes below the mud blanket, and the mud is pulled over the lip by a roller. The mud is then diluted and filter-pressed, the sweet water being used to melt the incoming raw sugar, and the press-cake is discarded. Various modifications of the Williamson clarifier have been devised and described[12, 36, 40, 61].

The Williamson system works extremely well. Its primary advantage, aside from simplicity and reduced costs[12, 36], is that it permits the use of phosphoric acid—lime defecation with the attendent large removal of color and colloids.

Phosphoric Acid with Inert Filter-Aids

In order to overcome the objections raised by critics of the Williamson system, many attempts have been made to gain the advantages of phosphoric acid in combination with the pressure-filtration system. The use of paper pulp as a filter-aid with phosphoric acid has been successfully, though not generally, carried out[44]. The addition of phosphoric acid in small amounts, together with filter-aids of high porosity, has been recommended for washed sugar liquors and affination sirups[17, 34]. This practice has not been generally adopted as it involves the expense of the filter-aid and filtration, together with the expense of the phosphoric acid. The use of both systems shows that the manufacturers of filter-aids have recognized the great advantage of phosphoric acid in refining, although for many years these advantages were denied or minimized. They are attempting to gain the advantage of both systems; that is, the positive filtration with filter-aids and the colloid and color removal of the phosphate treatment without heating the liquors to the high temperatures needed with the Williamson system. In this connection Robert Boyd[10] proposed the recovery of the filter-aid by an acid washing of the filter cake.

A recent patent[16] embodies the use of diatomaceous earth of graded particle size, mostly coarser than 10 microns, together with phosphoric acid and lime which has for its purpose the combination of the two systems. The claims for the patent are that the results are satisfactory as to rate of filtration, clarity of filtrate, and color removal.

Phosphate Treatment of Soft Sugars

A supplementary use of P_2O_5 more or less general in refinery work is the treatment of soft sugars with phosphoric acid. These soft sugars range from a very light yellow to a dark brown, have a soft grain and texture,

and are sold according to their colors, which are designated by numbers from 1 to 16. A small amount of dilute acid or monocalcium phosphate solution is sprayed on the sugar in the centrifugal, which results almost immediately in a marked brightening and improvement of the color of the product. The acid acts in several ways in this color improvement: by reducing the pH of the sirup on the crystals, by breaking up the salts of organic acids and releasing the volatile acids, and by precipitating the dark-colored organic iron salts as colorless phosphates. Aeration to remove fumes of organic acids is necessary before the sugar is packed. H. C. Welle[86] is generally acknowledged as the inventor of the phosphoric acid bloom treatment for soft sugars.

Bone Char Process in Cane Sugar Refining

Introduction

In addition to soluble phosphates, an important insoluble form is widely used consisting of a basic tricalcium phosphate mixture prepared from selected animal bones. This granular solid adsorbent is known as bone char and is used in commercial operations for the decolorization and purification of impure sugar solutions. This has been accomplished on a plant scale since about 1825 by passing the sugar liquors through the char contained in one of a number of filters 9 to 12 feet in diameter and 20 to 24 feet high. In a normal operating year approximately 10,000,000,000 pounds of raw cane sugar are refined in the United States requiring the use of about half of this weight of bone char. However, so enormous a quantity of bone char is not required since the char may be successfully and economically revivified many times. It is reliably estimated that in 1948 there were in the United States and Canada about 110,000,000 pounds of bone char in actual service.

The early history of the bone char process in sugar refining has already been reported[21]. Throughout the 125 years during which bone char has been utilized by the sugar refining industry there has been steady progress toward simplification in the chemical and mechanical operations. The acid and alkali treatment so prevalent in the early application of bone char in European beet sugar production has been entirely eliminated. Likewise, the fermentation step, which was conducted before the drying treatment, has been abandoned. The simplification became necessary because of the requirements of large-scale operations. The transition from small-scale operations to fewer refineries of larger capacity had the natural effect of stabilizing the refining procedure. In particular, the bone char process was standardized. The large investment by the refineries in the necessary stock piles of bone char has been one of the influences in the continued use of the process in cane sugar refining. Bone char also has advantages of sim-

plicity of operation, effectiveness as a purifying agent, and cheapness on a unit basis.

The details of operation with the bone char process vary considerably in different refineries. A number of factors influence the process but are not directly involved in the operations with bone char. Some of these are: (1) variations in the raw sugars; (2) the defecation technique; (3) relation of char and of vacuum pan capacity to the melt; (4) demand for specialty liquors, specialty sugars, softs, blackstrap, and barrel sirup; (5) quality of fine granulated sugars. Because of these variations the process can be discussed only in general.

Manufacture of Bone Char

Primary among the economic factors of the bone char process is the cost of the new bone char which must be continuously injected into the process in small quantities ranging from 15 to 25 per cent of the stock of service char per year. The crude bone for the manufacture of bone char is imported chiefly from South America. The majority of this tonnage is used in the manufacture of bone char, and a lesser quantity goes into the manufacture of glue. Bone after glue extraction is unfit for bone char and ultimately goes into cattle feed preparations. Table 1 gives the annual tonnage of these imports during the period 1938–1948 for the six major bone-exporting countries, namely, Argentina, Uruguay, Brazil, Mexico, Cuba, and Canada. Bone is also obtained in smaller quantities from Colombia, India, Siam, Australia, China, Libya, Madagascar, etc.

Although the cost of bone char is subject to fluctuations in the price of imported bone, it remains a comparatively cheap refining aid. Moreover, the revivification of char is accomplished rather inexpensively. Char can be revivified at an average cost of four to nine cents per 100 pounds, depending on fuel and other costs. Nevertheless, the total revivification costs are appreciable because of the large tonnage of char in process.

In recent years the cost of char has naturally increased, since it is dependent on the availability of the supply of bone, which in turn depends on world trade conditions. Recently, the cost of new bone char to the cane sugar refiner reached an all-time peak. In Figure 3 the cost of char (cane-sugar grade) has been plotted for the period 1905 to 1950 on the basis of data from several independent sources.

There are two processes used in the manufacture of bone char. The older practice is to heat the ground or cracked bones in a retort at 1000 to 1300°F from 9 to 12 hours. Apparatus commonly used consists of tubular vertical retorts about 12 inches in diameter set vertically in a furnace. Each retort extends through the top and bottom of the furnace. The operation is on the batch principle. The retort is filled with ground or cracked bones

introduced through the charge opening at the top. The charring operation is continued for 9 to 12 hours at the temperatures mentioned, depending on the type of bones charged and the quality of the char desired. The

TABLE 1. IMPORTS OF CRUDE BONE INTO UNITED STATES*

Year	Total (long tons)	Per Cent of Total from Major Bone-Exporting Countries					
		Argentina	Uruguay	Brazil	Mexico	Cuba	Canada
1938	20,142	44.9	17.0	8.7	3.2	15.0	7.1
1939	35,081	60.2	5.4	10.9	9.1	9.3	3.9
1940	35,677	57.4	4.4	6.4		12.6	
1941	77,703	45.3	2.0	7.1	0.4	22.0	18.9
1942	41,225	44.0	10.5	6.3	0.7	15.7	15.0
1943	34,764	41.1	15.5	4.9	0.8	25.3	9.4
1944	45,356	54.5	8.5	2.7	2.5	19.2	8.5
1945	41,007	52.2	5.5	2.2	1.6	17.8	13.1
1946	41,338	56.1	5.3	3.5	0.2	14.5	10.9
1947	60,230	62.6	1.8	4.3	0.6	10.8	7.8
1948	47,048	59.9	2.5	2.1	5.2	11.9	8.4

* "Foreign Commerce and Navigation of the United States," compiled by the Bur. of Census, U. S. Dept. of Commerce.
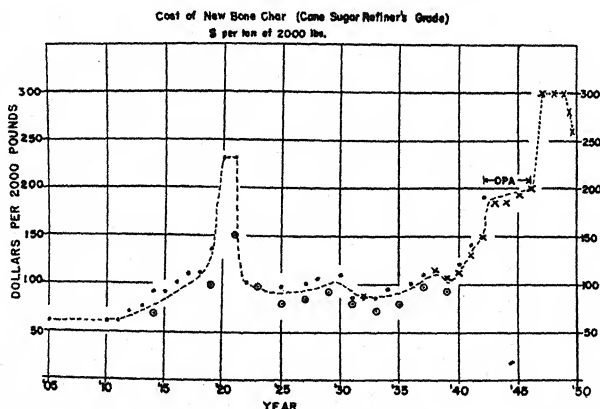
FIGURE 3. Cost of char (cane sugar grade) for the period 1905 to 1950.

volatile matter which is withdrawn through vents at the top of the retort is collected and treated for the recovery of such by-products as ammonia, tar, and fixed gas. Upon completion of the charring operation, the bone char is discharged through a gate at the bottom into drums. The effect on the quality of the char of the kind of bones used in its manufacture has been discussed by H. I. Knowles[45].

A continuous manufacturing process was introduced in 1932[83] which employed two rotary retorts in series. The ground or cracked bones are passed through an externally-heated rotary retort at a temperature of 900 to 1300°F for a period of from 1 to 2 hours, during which period the volatile matter is driven out of the bone. The material is then heated for a very short period (5 to 15 minutes) at a temperature from 1500 to 2000°F in the second rotary retort. The char leaving the second rotary retort passes through a cooler in which the char is cooled in the absence of air. The rotary retorts are arranged one above the other and the flue gases from the lower high temperature retort contribute to the the heating of the top retort. The advantages of the continuous process are reduction in labor, time of charring, and consumption of fuel as compared with the batch process.

A particularly promising synthetic substitute for bone char has recently been announced. The new material, called "Synthad," is formed from a mixture of a freshly precipitated basic calcium phosphate, a clay, and a carbonizable material. The mixture is extruded, dried, sized, and then carbonized in retorts in a manner similar to the treatment of natural bone[4]. Barrett and Brown[3] have designated the requirements of a substitute for bone char. The new adsorbent has been subjected to a detailed plant scale comparison with natural bone char[3] and the results have indicated that the synthetic material is a satisfactory replacement for natural bone, and in addition due to superior hardness, may reduce the make-up requirements of the bone char process by about 20 per cent.

Unit Operations

The bone char process may be considered to consist of six unit operations.

(1) Fresh or revivified bone char (about 45 tons) and the requisite amount of sugar liquor are introduced into the char filter. This process is generally known as "settling" the filter.

(2) A specified sequence of sugar liquors is passed through the char filter, an operation which may last anywhere from 30 to 130 hours depending upon the type of sugar liquors.

(3) The sugar liquor is replaced with water, the first stage of which consists in a displacement of the sugar liquor. This is then followed by an intermediate stage in which the sugar concentration rapidly diminishes. The latter stage is known as sweetening-off. The flow of water is continued in a final stage known as washing to the sewer. After the water has been drained from the filter the wet char is removed through a bottom door and distributed by means of a conveyor system into hoppers located on the floor below.

(4) This step is a drying operation in which the moisture is reduced from 20 to 25 per cent to 8 to 12 per cent.
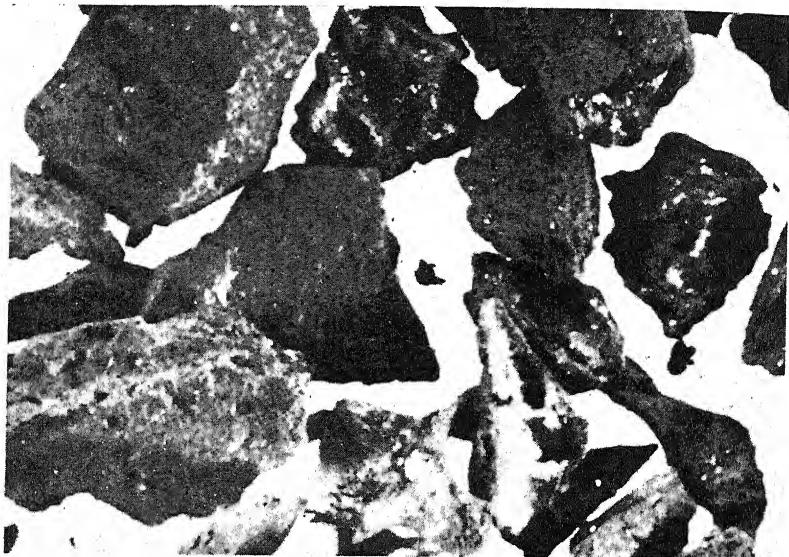
FIGURE 4. Individual granules of new natural bone char magnified 26.3 times have been found to retain the intricate and porous structure of bone.

FIGURE 5. Individual granules of used natural bone char magnified 26.3 times retained the bone structure but show the wear of the granules in the rounding off of the corners and edges.

(5) The char passes through the kiln where it is heated to a definite temperature for a specified time, after which it is cooled. The revivified char is returned to the filters by a vertical elevator system. The conveyor systems required to handle the wet and dry char may be classified as material handling and constitutes the sixth unit operation.

Settling of Char Filter. The settling of a char filter is accomplished in three different ways. In dry-settling the filter is filled with dry revivified char and the sugar liquor then introduced. The two other methods are known as wet-settling. In one of these the filter is settled by the simultaneous addition of bone char and sugar liquor. The other method consists in filling the filter about two-thirds full of sugar liquor and then adding the dry char. The quantity of liquor and the addition of char are chosen so as to end up with a filter filled with char completely covered by liquor.

The distribution of the particle sizes of the char in the filter is of great importance, and this is thought to have considerable influence in the resulting flow through the filter. The influence of the particle size of the char on the decolorizing power has been discussed by de Whalley and Albon[28]. Dry-settling has been observed by H. I. Knowles[43] to result in pronounced channeling and significant differences in the time of contact between the char and the flowing liquor. There is a definite temperature rise which is attributable to the release of the heat of wetting of the dry char by the water contained in the sugar liquor. De Whalley and Dickinson[29] have determined the heat of wetting by water and by 60°Brix sugar liquor and report that the presence of the sugar did not affect the heat of wetting. Despite the complications of dry-settling and its possible shortcomings, it is a necessary operation in starting up a refinery after week-end or other shut downs.

In the majority of operations one of the two methods of wet-filling is practiced. In the simultaneous addition of the char and liquor, both are fed continuously to some mixing device located in the neck of the filter. The ratio of char to liquor is regulated so as to form a viscous mixture which then falls into the filter. It is believed that the segregation of the large from the small particles is prevented by the high viscosity of the mixture.

The second method of wet-filling is sometimes known as the drowning process. After the filter has been filled to about two-thirds full with sugar liquor, the dry char is added. Whereas there is undoubtedly some segregation of the various sizes of char particles as they settle to the bottom of the filter, in the opinion of some operating men, that channelling is largely eliminated by either of the two wet-filling processes.

Either method of wet-filling char filters usually requires that a portion of the filter at the bottom be filled with dry char. This apparently serves two purposes: (1) to keep the filter blanket in place and, (2) to help pro-

duce a clear initial liquor instead of a hazy liquor which necessitates a refiltration. In recent years the conventional cloth blankets have been replaced by metal screens. Filters so equipped do not require the addition of a footing of dry char, except where it has been found necessary to prevent the formation of a hazy liquor.

Filtration Operations with Sugar Liquors. It should be noted that the bone char process is located in a position about midway in the refining procedure. A typical flow diagram for cane sugar refining is illustrated in in Figure 2[76]. The operations before the bone char process include the material handling of the raw sugar, the removal of the film of molasses which surrounds the individual grains of raw sugar (affining), the solution of the washed raw sugar (melting), and the defecation of the resulting sugar liquors. After the bone char process, there are the operations with the vacuum pans, the centrifugals, drying and screening of the sugar crystals, and the packaging of the sugar products.

The quantity and quality of the sugar liquors introduced to a char filter vary considerably in different refineries. In general, the best decolorization and ash removal is attained in the early stages of flow through the char filter. The usual procedure is to settle the filter with once-filtered high-test sugar liquors (i.e., liquors for refiltration) and to run for a definite period of time using the same material. This is followed by a grade of material known as washed sugar liquor which may or may not contain remelt sugar liquor. When this grade of material begins to deliver liquor of a yellowish coloration, instead of nearly water-white, it is generally sent through another char filter for refiltration. It is then customary to introduce into the filter a material of intermediate purity. This is followed by sugar liquor of the lowest purity to be char-filtered.

In addition to purity consideration, the sugar liquors intended for char filtration are specified by their density (°Brix), pH, color, ash content, and temperature. The Brix is usually in the neighborhood of 60 to 65° and the temperature about 160 to 180°F. All efforts are made to maintain the pH of the liquors on the char filter in the vicinity of 7.0. The pH changes are influenced greatly by the electrolytes contained in the liquor as recently shown by K. Löwy[54] and C. W. Beal[6]. The density of the lower-purity liquor is usually adjusted to be somewhat less than those of highest purity and the temperatures also increased somewhat. The influence of anions on the decolorization of sugar liquors by bone char has also been investigated by K. Löwy[55]. The decolorization of Chinese raw sugars by bone char has been discussed by Li, Chang, and Liu[51].

Operations with Water-On. After the allotted quantity of sugar liquor has passed through a char filter, the supply of liquor is replaced by hot water at about 200°F. The accepted procedure has been to postpone the

addition of water until the level of the sugar liquor recedes into the top level of the char. However, a recent innovation has been proposed in which the water is added immediately without baring the char[5].

During the process there is a certain amount of mixing of the sugar liquor with the water to form sweet water. It is advantageous and often very necessary to keep the volume of this mixture at a minimum. The formation of sweet water is caused in general by turbulence, diffusion, liquor adhering to the outside of the particles, and liquor within the pores of the bone char particles.

In order to minimize the mixing of the sugar liquor and water, the flow is usually reduced. The old trickling practice[2] used rates of liquor flow of 80 to 100 cu ft/hr. Modern char houses operate at flow rates which may average 200 to 300 cu ft/hr. The run-off from about 40 Brix to 3 Brix or lower is usually collected for multiple-effect evaporation. At a predetermined point, the exit water is directed to the sewer.

Greater attention in present practice is given to the water washing of a char filter. A. B. Babcock[11] has made a study of the elimination of mineral salts in cane sugar refining. He states that the point where the washing of bone char ceases to be economic is independent of the volume weight of the char and recommends that all chars be washed to the same final value for ash content of the wash water. Evidence is adduced to show that the kilning of the char appreciably increases its ash-removal property. Results of experiments made by Jean Salsat[73] indicate that the char should be sweetened-off with very hot water at pH 7 to 8, the exit runnings not falling below 165°F. If the pH drops below 7.2 during the operation, Salsat recommends that NaOH or Na_2CO_3 be added to the water used for further washing.

Lyle[57] has described a method of conducting operations in which the water is directed through several char filters in series. One of the expected and unavoidable results of the water operation in general is the presence of bacterial action in the diluted sugar liquors in the char filter. The low density sweet waters are always maintained at a sufficiently elevated temperature to avoid such bacterial action.

Drying of Washed Char. The moisture in the washed spent char ranges between 15 to 25 per cent on a wet basis. This moisture must be removed before the temperature can be raised to the point where the desired chemical reactions take place[27].

Commercial driers for bone char have been described in a recent review publication[22]. Modifications on the original Farley drier of 1871[32] may be arranged in the following chronological order: Eastwick, Scotch (Blake-Barclay), Newhall, Deeley, Kent, and DeVries. In all of these driers the char descends by gravity in a curtain on the outside of an A-frame structure.

In the Buchanan kiln the drier is simply an extension of the vertical retort (about 1-foot diameter) within which is located a vent pipe for removing the moisture. These retorts are externally heated.

In general, the amount of water removed in the dryer is only sufficient to reduce the moisture content from 15 to 25 per cent to 10 to 15 per cent. In older drying equipment the heat transfer is realized by an indirect exchange between the char and the metal walls heated by flue gases from the kilns. The DeVries drier, illustrated in Figure 7, improves the efficiency of moisture removal as well as the exchange of heat. Bemis and Reed[7] have studied the operating characteristics of the common types of com-
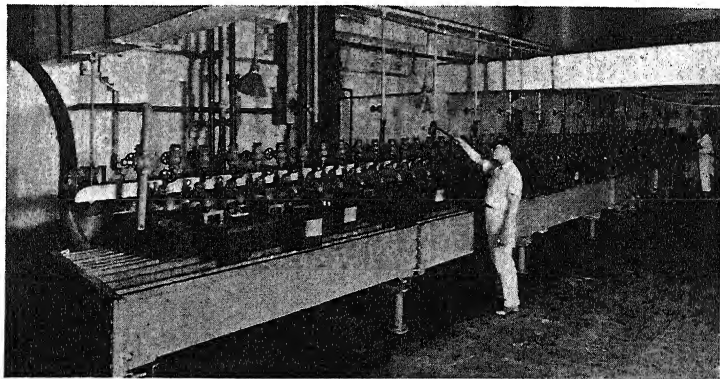
FIGURE 6. Liquor gallery at the Western Sugar Refinery, San Francisco, Calif. Each outlet valve is connected to a separate filter and the flow from each may be directed into any one of a number of troughs.

mercial char driers. The over-all drying rate for several types varied widely from as low as 0.1 to almost 3.0 pounds water/hour for each square foot of char exposed.

Kiln Operations. The refineries of the United States, with one exception, are equipped with kilns with stationary vertical retorts. The exception is the Herreshoff furnace adapted by the Refined Syrups and Sugars, Inc. to a char kiln. Buchanan and Scotch kilns are used in Australia, Canada, England and South Africa. The kilns with vertical retorts may be classified in two groups: namely, the Scotch kiln and the U. S. char kiln. The former is chiefly characterized by three rows of vertical retorts arranged on both sides of the fuel bed which extends along the length of the rows; the U. S. char kiln has but two rows on both sides.

All of the Buchanan kilns have a double row of retorts on either side of the fire, the rows containing 6 and 5 retort assemblies, respectively.

Each retort (12 inches in diameter) delivers the char into a cluster of 7 cooler pipes and the entire assembly of drier, retort, and cooler rotate slowly so as to present all sides to the radiant heat of the fuel. The Buchanan and Scotch kilns are equipped in general with cast-iron retorts, but a greater part of the industry in the United States and Canada has now been converted to thin-wall stainless steel retorts (Figure 8).

The combustion chamber occupies about one-quarter the width of the
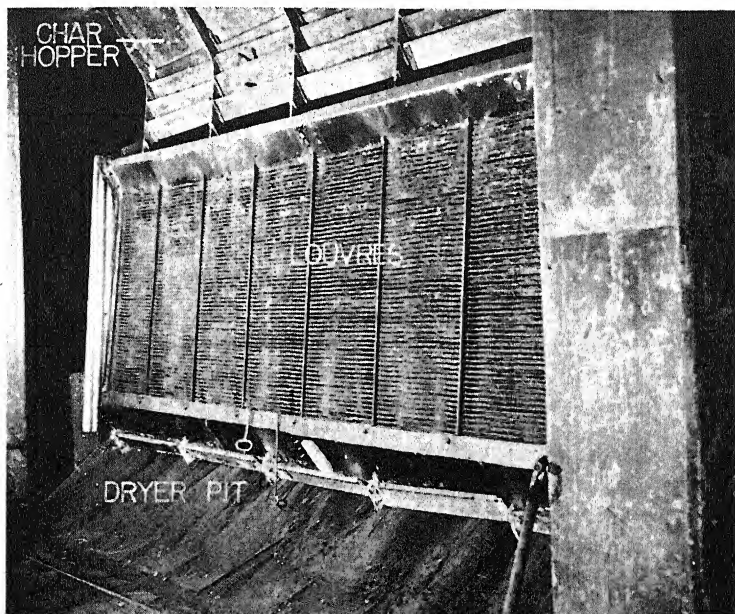
FIGURE 7. Drying bone char.

kiln and runs through the entire length. It may be fired either from one end or from both ends. Fuel for heating char kilns includes the four available types: coal, oil, natural gas, and coke. The temperature of the kiln atmosphere surrounding the retorts may vary from 900 to 1100°F. In general, the kilns with thin-tube retorts have the lowest kiln-air temperature. The location of the thermocouples to read and control the kiln-air atmosphere varies considerably, the preferred location being between the rows several feet below the ceiling.

The decarbonization of service char was once a serious problem in the maintenance of a char stock of high efficiency. A rotary kiln of the Weinrich design[8] was once widely used and several are still in service. Since a

single decarbonizing unit can handle only a small portion of the char being revivified, it was not possible to realize the maximum benefit of decarbonization for the entire char stock[8]. In recent times there has been considerable experimentation in decarbonizing char as it passes a controlled opening at the top of the cooler pipes in the United States stationary kilns. This method is an inexpensive way of maintaining the desired average value for per cent carbonaceous matter in the char. Some of the fundamental aspects of the reaction of oxygen with bone char have been recently reported[52, 53].

The cooling of char in kilns with vertical retorts is realized with either single- or triple-cooler pipes made of sheet iron and extending about 8 feet below the kiln. The cooler pipe takes the char at 1000°F and cools it to the point where it can be released to the atmosphere without burning the carbonaceous matter.

The mechanisms employed to draw the char slowly through the retort and cooler combination are of five types: the Buchanan draw, the bucket type, the ladder type, slotted plates, and a movable plate beneath a stationary adjustable blade[22]. The average draw is of the order of magnitude of 40 cu ft per kiln hour or about 0.6 cu ft per retort hour. The flow of char through the retorts on various rows and at various locations in a given row is sometimes varied in order to compensate for the lack of uniform heat distribution in the kiln.

The adaptation of the Herreshoff furnace to serve as a char kiln[35] represents a mode of revivification completely independent of the conventional char kiln. Direct contact of the flue gases with the char is made during both the drying and kilning stages. The recirculation of flue gases through the external combustion chamber serves to limit the maximum temperature of the gases in contact with the char, and the volume of these gases aids in the heat distribution and drying operation. This kiln has been successfully used at the Refined Syrups and Sugars, Inc.

Material Handling. Millions of pounds of sugar liquor and bone char move daily through the char house. The conveyors and buckets to handle the char are of the usual design. Common practice is to install a magnetic separator for the removal of tramp iron on the char belt located directly beneath the cooler pipes. The mechanical handling subjects the particles of bone char to unavoidable attrition. The fine dust is usually removed by means of suction fans at the top of the char elevators. The distribution of char at the top of the filters is usually associated with sieving devices to remove particle sizes below a No. 50 sieve. The screening of the various grades of service char is a very important adjunct to successful operations in the char filter.

The use of a mechanical separator to remove char particles of different

Labels in images: Inclined Plate · Vapor Box · Fire Arch · Pyrometer Sleeve · Oil Flame · Monolithic Furnace Cement

(1)   (2)   (3)

(Courtesy of Dan Gulleben)
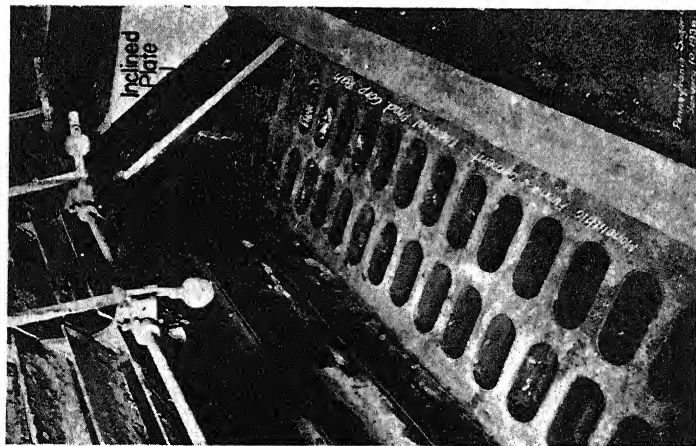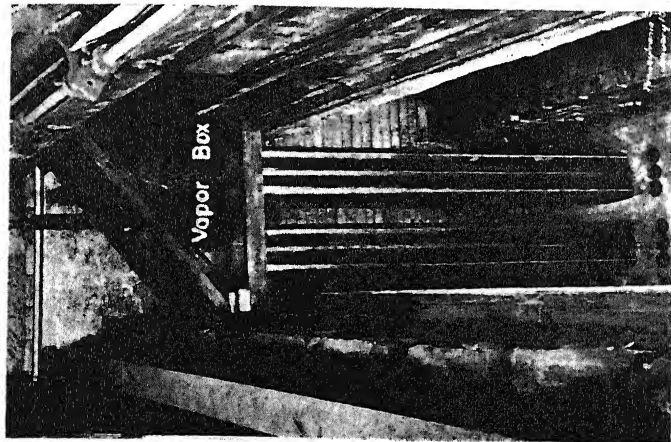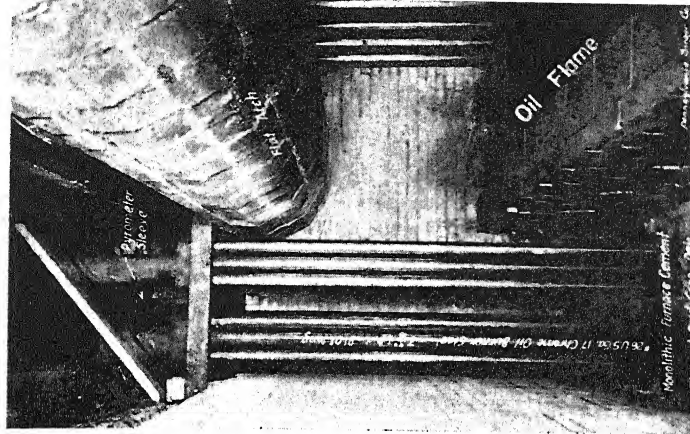
Fig. 8. Installation of thin-tube retorts in a char kiln. (1) View of the top of the retorts beneath the inclined plate taken during construction; (2) View taken during the installation of the three-tube stainless steel retorts; (3) Side view during construction showing the flat arch, flame and baffles between the retorts.

densities has been adopted generally in almost all char houses. This method was originally described by Brown and Bemis in 1934[11]. It consists of an adjustable screened deck through which air passes at a rate of 1,700 to 3,100 cu ft/minute. The separator deck resembles a mining concentrating table deck in that baffles 1 inch apart run the length of the deck. The deck may vibrate $\frac{3}{16}$ inch longitudinally 330 to 400 times per minute. Brown and Bemis state that the table operates best at a feed of 3,000 lb/hr, with a discard rate of 3 per cent and dust removal of 1 per cent.
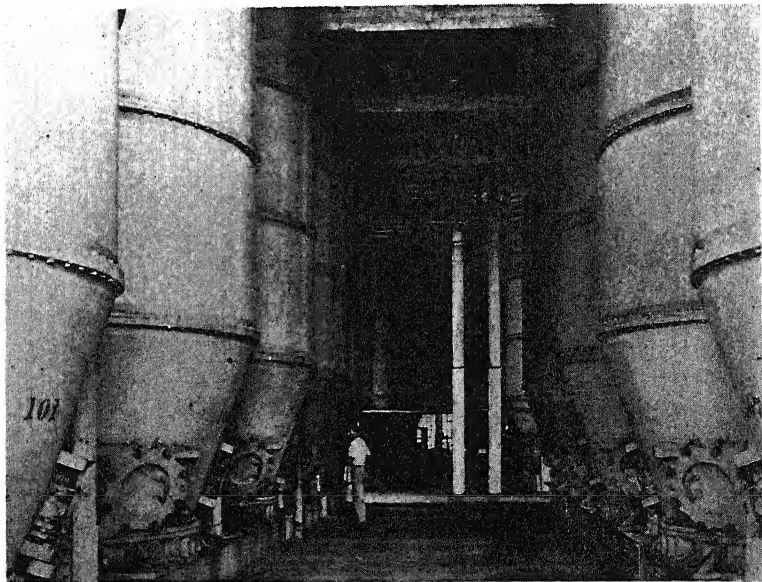
FIGURE 9. An installation of char filters in a cane sugar refinery.

Test Procedures

The test procedures in common use are described in the "Spencer-Meade Handbook"[76]. The accurate determination of the carbon content is described in a paper by Deitz and Gleysteen[25], and that for sulfur in its several forms is contained in a paper by Deitz, Higginson and Parker[26]. The control tests employed in French refineries have been reported by Salsat[72]. G. P. Meade[60] has described a procedure to determine the weight per cubic foot of refined sugar in which a simple apparatus is proposed. The method is applicable to other granular substances and has been proposed to determine the weight per cubic foot of bone char. A survey of the analytical laboratory methods for evaluating bone char and other adsorbents has been made by V. R. Deitz[23].

U. S. patents dealing with bone char technology are listed in Table 30 of the Appendix.

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28. Phosphates in Flame-Resistant Products

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INTRODUCTION

Records of attempts to fireproof fabrics date back as far as 1638[22]. The use of ammonium phosphate for this purpose was suggested in 1786, but apparently the first systematic investigation on the fireproofing of fabrics was undertaken by Gay-Lussac in 1821[10]. He compared the fire resistance of strips of fabric impregnated with various salts and concluded that the most effective were those that had a low melting point and evolved non-flammable gases on heating. Phosphate salts either alone or mixed with other compounds were found to be among the better fire retardants.

Great progress was made in developing fire retardants during World War I and in the period immediately following[4, 17, 20], but it may be said that no coating or impregnating solution has yet been found that will render organic fibrous materials fireproof in the strict sense of the word.

As Buck[3] states, all cellulose fibers are combustible and the degree of flammability depends in a large measure on the form in which cloth is fabricated. There are, however, compounds that may be applied which lower the combustibility of woven materials and thus greatly reduce fire risks. Certain derivatives of phosphoric acid have outstanding fire retardant properties and though organic fabrics impregnated with them may char and burn slowly when highly heated, they are not readily ignited; when the source of heat is removed they cease to flame and do not exhibit the so-called after-glow or slow combustion, which can almost completely destroy the fabric. Such protective materials are more properly termed flame resistant.

Whereas the problem of adequate flame resistance has not been completely solved, innumerable lives could have been saved and the destruction of untold wealth prevented, had our knowledge of fire retardants been properly applied and reasonable precautions taken to reduce the combustibility of organic products by methods of treatment already established.

Legislative Restrictions

In recent years, however, the public has been so thoroughly aroused by certain disasterous fires that safety authorities are demanding more adequate laws to prevent their recurrence. Legislative restrictions on the use of flammable materials in public places now exist in 25 states, and though they vary somewhat in each state, a pattern is being developed which it is hoped will be universally adapted. The National Board of Fire Underwriters[19] has recommended the following ordinance which is favorably regarded by most legislative bodies:

"2 Decorative Materials

   (a) All decorative material, including curtains, acoustical materials, streamers, cloth, cotton batting, straw, vines, leaves, trees and moss, but not including floor coverings shall be rendered flameproof; provided this shall not be required of materials not exceeding one-sixteenth inch in thickness applied directly to and adhering to a non-combustible base. Such flameproofing unless certified by Underwriters' Laboratories, Inc., or other laboratories of recognized standing, as being of a permanent nature, shall be tested by the fire department each six months and the treatment renewed if necessary.

   (b) The use of imitation leather (or other material) consisting of or coated with a pyroxylin base is prohibited.

Flameproofing products may consist of one or more compounds. Generally speaking they fall into the following two broad groups:

   (1) Temporary or soluble products which may be washed out with soap and water.

   (2) Permanent or insoluble products which may be applied as such, or formed by chemical reactions upon or within the body of the material treated."

Each of these two classes of flameproofing products meet somewhat different specifications: Those of the temporary type are usually applied to clothing and decorative textiles and though they should adhere tightly to the fibers they must not weaken the fabric, affect its color or so stiffen the cloth that its draping qualities are impaired. In the case of wearing apparel the flame resistant application must not irritate the skin or cause discomfort due to moisture absorption, air permeability and heat conductivity.

On the other hand, so-called permanent flameproofing compounds are designed to withstand weathering conditions and must not deteriorate markedly when exposed to the leaching action of rain and subjected to rather abrupt changes in temperature. Flexibility of such coatings is often an important factor but they need not necessarily maintain the original softness and draping qualities of the textiles.

Action of Flameproofing Products

The action of flameproofing compounds has been explained in the following ways:

(1) Fusion of the product before the ignition temperature of the fabric is attained, thus causing coatings more or less impervious to air.

(2) Evolution on heating of non-combustible gases that tend to extinguish flame.

(3) Reaction between the applied flameproofing agents and the fibrous cellulose to form relatively nonflammable products.

(4) Absorption of heat of flame by some chemical change.

(5) Dissipation of heat of flame by conduction.

Of the five suggested explanations the first three appear to have supporting evidence:

(1) Sodium and ammonium phosphates decompose at elevated temperatures yielding water and ammonia. Neither of which support combustion. The various reactions involved on heating such salt are given below:

$$2NaH_2PO_4 + Heat \rightarrow Na_2H_2P_2O_7 + H_2O$$

$$2Na_2HPO_4 \cdot 12H_2O + Heat \rightarrow Na_4P_2O_7 + 14H_2O$$

$$Na_2H_2P_2O_7 + Heat \rightarrow 2NaPO_3 + H_2O$$

$$NH_4NaHPO_4 + Heat \rightarrow NaPO_3 + NH_3 + H_2O$$

$$NH_4H_2PO_4 + Heat \rightarrow HPO_3 + NH_3 + H_2O$$

$$(NH_4)_2HPO_4 + Heat \rightarrow HPO_3 + 2NH_3 + H_2O$$
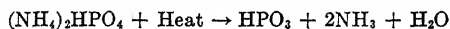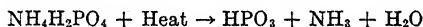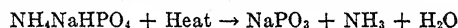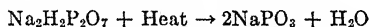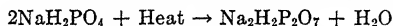
(2) The residual products obtained, according to the reactions given above, are fusible compounds that tend to form glazes thus further protecting the surfaces of combustible materials from the flame.

(3) Some flameproofing agents are blended with a view to reacting with the organic fibers and forming products that are less combustible than the original cellulose. Fire retardants apparently induce the decomposition of cellulose fibers to carbon and water, resulting in a decrease in the quantity of tar and flammable gases evolved[13, 20].

Gulledge and Seidel[13] have devised a technique for determining the proportions of char and volatile matter formed when textiles treated with various fire retardants are heated to their decomposition temperatures. The procedure employed is as follows:

"A portion of a vertical borosilicate glass tube is heated to the indicated temperature by a surrounding furnace and nitrogen gas is swept through continuously from top to bottom. When all is in readiness, the sample is dropped from the cool upper portion of the tube into the hot area. No

oxygen is present and the nitrogen sweeps the products of pyrolysis through glass wool which traps the tars. Water is collected in a dessicator tube and carbon dioxide in a lime tower. The charred residue is weighed." Table 1 shows the results obtained by applying this test to samples of cotton treated with various flameproofing agents.

Temporary Flame-Resistant Phosphate Products

It was noticed long ago that old timbers which had been used in buildings where phosphoric acid as manufactured and which became impregnated with phosphate compounds could only be burned with great difficulty. The resistance to fire of such ordinarily readily combustible materials sug-

TABLE 1. EFFECT OF TYPICAL FLAME RETARDANTS ON THE DECOMPOSITION
PRODUCTS OF COTTON

Flame Retardant	Temp. (°C)	Products (%)			
		Char	Tar	H_2O	CO_2
$(NH_4)_2HPO_4$ (14%)	550	36	22	39	5
$(NH_4)_2HPO_4$ (14%)	350	45	7	47	4
Borax-boric acid (13%)	500	41	5	40	9
Borax-boric acid (13%)	350	57	1	33	8
Ti/Sb (10%)	500	37	12	35	6
Ti/Sb (10%)	350	49	5	37	7
Control	500	8	54	29	6
Control	350	12	42	33	6

gested the idea of employing solutions of phosphoric acid or soluble phosphates to treat fabrics and wood in order to render them flameproof. Since phosphoric acid attacks and weakens organic fibers the salts of this acid appeared to be the most logical compounds to use for flameproofing purposes.

Whereas, most of these phosphate salts do not detract from the strength of the fabrics except when the impregnated products are heated or exposed to sunlight for protracted periods, they do tend to crystallize and slough off when the fabric dries out, thus affording only partial protection.

In order to increase the adherence of phosphate salts, other compounds are frequently added which reduce or prevent the formation of crystalline products and add desirable physical properties to the flameproofing product. Boric acid, borax and sodium silicate have been used for this purpose with considerable success. Various other substances are often added to prevent or reduce rot and inhibit the growth of bacteria.

Ferguson[8] patented a flameproofing solution of the following compo-

sition:

	parts
Sodium silicate ($Na_2S_4O_9$)	143
Borax ($Na_2B_4O_7 \cdot 10H_2O$)	10
Microscosmic salt ($NaHNH_4PO_4$)	10
Monosodium phosphate ($NaH_2PO_4 \cdot H_2O$)	4
Water	100

Sodium silicate is used in this mixture because of the refractory nature of the glaze which it forms; borax is employed because of its well-known property of fusing to glass at high temperatures. The inventor also claims that borax aids in distributing the fireproof film of sodium silicate. In addition to the fact that the phosphate salts have fireproofing properties, sodium ammonium phosphate gives off ammonia when heated, and it is claimed that this ammonia is held for a short time beneath the fireproof film of sodium silicate and borax, serving not only to extinguish the flame but also the smoldering embers.

With the idea of overcoming the tendency of phosphate salts to crystallize and drop from the fabric, Andrews and Mathias[1], after a series of investigations, proposed the use of solutions containing monosodium phosphate and borax or disodium phosphate and boric acid, so proportioned that the dried mixture is noncrystalline and has a pliable or colloidal nature which causes it to adhere to fabrics without stiffening them. These investigators used the phosphates of soda instead of ammonia on fabrics particularly, because the latter salts tend to lose ammonia and the fireproofing compound not only becomes less effective, but gradually assumes an acid nature which deteriorates the fiber and adversely affects the color of dyed materials.

Cobbs[5] patented a process for flameproofing textiles and various other combustible products comprising impregnating them with either monoalkyl or dialkyl ammonium phosphate or a mixture of such organic phosphates along with monoammonium phosphate in aqueous solution. The excess solution is removed by wringing and the treated fabric dried. The inventor claims that textiles so treated are softer and more flexible than the original materials and that no objectionable crystalline deposits are formed. Cobbs describes methods of preparing the organic phosphates but does not claim that these form part of his invention. Apparently material thus treated cannot be washed without losing its flameproofing properties.

According to Fain[7] the National Research Council Laboratories at Columbia University after intensive study of water-soluble flameproof materials, recommended the following rather simple formula to the Army

Quartermaster Corps for use on clothing:

Borax	7 lbs
Boric acid	3 lbs
Diammonium phosphate	5 lbs
Water	110 lbs

The material to be flameproofed is dipped in the above solution until thoroughly impregnated and then dried. The procedure may be repeated several times depending on the character of the fabric and the degree of flame-resistance desired. Quantities of the dried mixed salts ranging from 7 to 15 per cent of the weight of the fabric have been found effective.

METHODS OF APPLYING WATER-SOLUBLE FLAME-RESISTANT COMPOUNDS

Since water-soluble phosphate salts can be applied to textiles in the form of solutions their uniform distribution on cellulose and other types of fibers is relatively simple.

The most effective way of impregnating textiles with such salts is by immersion, followed by wringing and drying. Little *et al.*[17] state, however, that many of the more common fire retardant mixtures will hydrolize or decompose at elevated temperatures. They advise that caution be exercised in drying or ironing textiles impregnated with ammonium phosphate so that ammonia will not be evolved and the fabric injured because of the acid nature of the residual salt.

In some cases it is desirable to apply the flameproofing agent by spraying. In this way curtains, draperies, etc., may be treated without taking them down. Little *et al.*[17] describe this method as follows:

"The fabric is hung up and thoroughly sprayed with a highly concentrated retardant solution until it appears definitely moist. Any suitable spraying equipment may be employed; however, in order to avoid streaking of the fabric on drying, the spray should be as fine as possible. With heavier fabrics it is often necessary to apply the spray to both sides of the cloth. The method in general suffers from a tendency to produce uneven distribution and requires some experience to achieve a satisfactory treatment. In treating curtains and garments in the home, a modification of this technique can be used by applying the retardant when sprinkling just before ironing. The cloth must be thoroughly moistened, however, and the fabric should be allowed to become nearly dry before ironing in order to avoid undue decomposition of the flameproofing agent."

For a description of the method of impregnating fabrics with soluble flameproofing agents in commercial laundries the reader is referred to the excellent article mentioned above.

PERMANENT FLAME-RESISTANT PRODUCTS

It is obvious that no water-soluble salt is suitable for flameproofing textiles exposed to weathering influences unless it is protected by some impervious coating. Such a coating may combine with other added compounds to form insoluble, fire-resistant products within the body of the fabric, or may act directly upon the cellulose itself changing the combustible nature of the fiber so that it can be washed without losing its flame-resisting properties.

These types of fire retardants are required for treating canvas and textiles used in the manufacture of tents, awnings and outside covers, subject to the leaching action of rain. Such fabrics are also often treated to render them water repellant and resistant to attack by insects and mold.

Titanium and antimony compounds are used to a large extent in these so-called durable fire-resisting coatings[13], but both organic and inorganic compounds of phosphorus also play an important role in such products.

An outstanding example of where a fabric should be both water-proof and fireproof is in the wings of the cheaper types of airplanes. In order to render such fabric impervious to air and moisture, it is customary to coat it with such substances as pyroxylin or acetyl cellulose, which not only renders the material waterproof, but causes enough shrinkage to tighten the fabric on the frame. These coatings, however, are highly flammable, which adds greatly to the hazards of aviation and hence a method of fireproofing or lessening their flammability is of considerable importance.

Lindsay[15] proposed the use of both an organic and inorganic phosphate for this purpose. The materials employed and the method of application may be briefly described as follows:

The fabric is first fastened to the airplane frame and a solution of ammonium phosphate applied with a brush till the fibers are thoroughly impregnated with the salt. After drying, the following solution is applied to the cloth.

	parts
Pyroxylin	100
Tricresyl phosphate	50
Acetone	300
Methyl alcohol	600
Amyl acetate	300

Several coats of this solution may be used if necessary to obtain the desired effect.

Tricresyl phosphate is said to materially reduce the flammability of the pyroxylin. This type of coating, even without the addition of the ammonium phosphate, is therefore safer than that previously employed.

The presence of fine crystals of ammonium phosphate in the fibers of

the cloth, however, and their distribution through the mass of pyroxylin increases still further the fireproof properties of the fabric.

Since the ammonium phosphate is coated with the waterproof pyroxylin the inventor claims that there is no danger of the salt being washed away or lost on exposure to the weather.

Since organic materials are associated with combustibility, their possibilities as flame-retardants were not considered for many years. Now, however, a number of organic phosphorus compounds such as the diphenyl

FIGURE 1. Flame-retardant properties of organic phosphate plasticizers can be compared in finished plastic compositions.

or diethyl esters of phenyl phosphoric acid[23] and tribromo and trichloromethyl phosphate[6] have been added to the list of flameproofing products (Figure 1).

As further evidence of the trend towards organic phosphate derivatives, McLean and Marrian[18] obtained a patent on a process for the more or less permanent flameproofing of cellulose materials, which comprised impregnating the materials with polyetheleneimene and then treating the impregnated product with an aqueous solution of the reaction product resulting from the interaction of dipentaerythritol, orthophosphoric acid, and phosphorus pentoxide. It is claimed that the addition of the latter solution to the impregnated textile results in a flameproofing reaction product which anchors itself so firmly to the cellulose fibers that the fabric

(after being heated to 100°C) may be washed with soap and water without losing its flame-retarding properties.

In a patent issued to W. E. Gordon[12] the inventor claims a permanent flameproofing product for textiles and the process of producing the same. This process consists in impregnating a cellulose fabric with 8 to 20 per cent of its weight of polymeric ethylenimine, baking the material, and then impregnating the fabric with an amount of phosphoric acid sufficient to retard combustion.

Thomas and Kosolapoff[21] describe a method of treating textiles in which the cellulose fiber itself is converted into a flame-resistant product. In this process no inorganic salts are employed, but the textile is reacted with phosphoryl chloride in the presence of pyridine at a temperature of about 70°C. The reaction product is then treated with ammonia gas resulting in a complex cellulose derivative containing nitrogen and phosphorus which not only is a flame retardant but will not leach out when the fabric is washed with water.

Leatherman has taken out several public service patents[14] dealing with compositions of matter for rendering fabrics both rot-proof and flame-resistant consisting of five constituents dissolved in suitable solvents to permit the ready impregnation of the cloth or textile. The proportions of materials may be varied but one typical formula is as follows:

Vinyl acetate—vinyl chloride copolymer	15 lbs
n-butyl methacrylate	5 lbs
Tricresyl phosphate	7 lbs
Triphenyl	7 lbs
Zinc oxide	27 lbs
Organic solvents (acetone, etc.)	54 lbs

It is claimed that elasticity, toughness and other desirable properties are imparted to the mixture by the resins and the plasticizers (tricresyl and triphenyl phosphates). The inventor states that when the fabric coated with this solution (containing suspended solids) is subjected to ignition temperatures, the decomposition of the products frees gases and vapors that act as flame retarders. It is further claimed that mixtures of these various materials can be successfully used in flameproofing cotton, silk, wool and rayon.

Among the more durable fire retardant products for treating textiles, the urea-phosphate types have proved very effective in promoting the desired flame and glow resistance[16].

Whereas, urea alone has little value as a flameproofing agent and phosphoric acid cannot be used because of its deleterious action on cellulose fibers, mixtures of these two compounds have proved quite suitable for impregnating textiles.

Essentially this process involves a reaction at elevated temperatures between the three constituents (urea, phosphoric acid and cellulose) whereby complex insoluble cellulose esters are obtained. In actual practice the fabric is immersed in an aqueous solution containing urea and phosphoric acid (in the ratio 1:1) until thoroughly impregnated. It is then dried, cured at an elevated temperature (150 to 200°C) to promote esterification and finally washed with water to remove any unreacted components.

Fabrics containing 12.5 to 15 per cent of the urea-phosphate mixture exhibit excellent flame-retardant properties and are resistant to leaching by water.

Ford and Hall[9] propose a method for permanently fireproofing textiles. This consists in treating the textiles with a solution made up of phosphoric acid, urea, a volatile decomposible alkaline reagent (ammonium hydroxide) and formaldehyde. The following is a typical formula of a solution said to be well adapted for rendering cellulose materials flameproof:

Phosphoric acid (75% H_3PO_4)	100 lbs
Urea	200 lbs
Ammonium hydroxide (25%)	15 lbs
Formaldehyde (37%)	50 lbs
Water	100 lbs

The inventors state that the formaldehyde has a strong affinity for the nitrogen compounds, and when the solution is applied to fabrics, fire-resistant organic complexes are formed in the cellulose fibers. After drying and curing it is claimed that the fabrics so treated may be washed or dry cleaned and still retain their flame-resisting qualities.

Flammability Tests for Fabrics

Church *et al.*[4] describe in detail the various tests for evaluating flameproof fabrics, but the method most commonly used for testing flame-resistance is known as the vertical-bunsen flame test. This is conducted in a cabinet, front and side views of which are shown in Figures 2 and 3.

The authors describe this test as follows:

"Three or more 2 x 12 inch specimens are cut from the sample of treated cloth, with the long dimension in the direction of the warp, and conditioned for 48 hours at 70°F/65 per cent relative humidity before testing. In mounting within the cabinet the specimen is held in a suitable clamp at the top and the bottom edge positioned 0.75 inch directly above the top of the burner, with the lower corners held under slight tension. By use of a quick-acting valve and a butane-air mixture for the burner, a slightly luminous flame 1.5 inches high is applied to the lower edge of the suspended fabric specimens for exactly 12 seconds. A small pilot light, attached to the

burner through a swivel joint to allow it to be moved out of position while adjusting the specimen in place, is recommended for better defining the exact time and extent of ignition. With the extinguishing of the burner
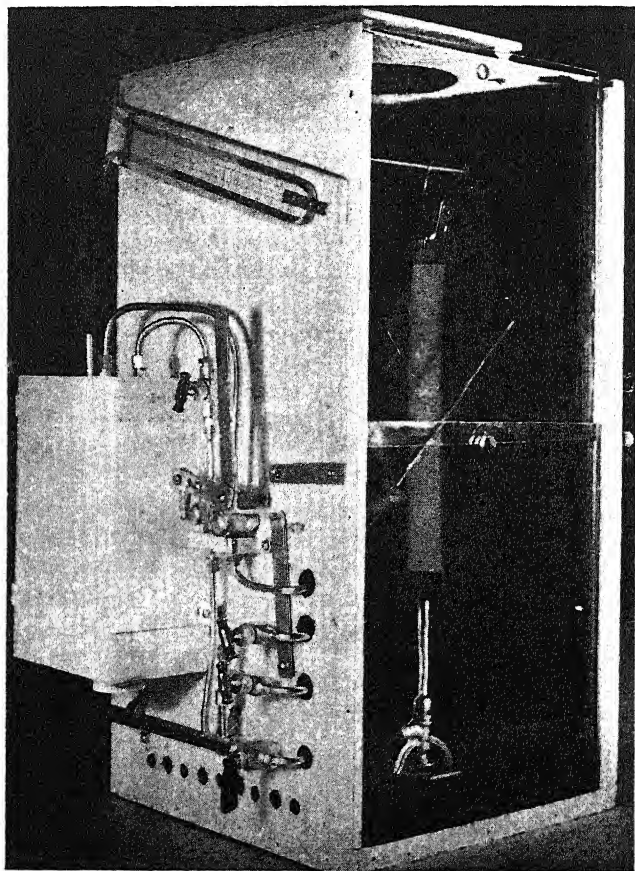
FIGURE 2. Equipment for evaluating flame-proofed fabrics. Side view of cabinet showing connections for introducing and controlling flow of gas to bunsen burner.

flame, observations are made with a stop watch, noting the time in seconds of the after flaming, and the time of afterglow once the flaming has ceased. The length of char produced by the combined flaming and afterglow is measured in 0.1 inch from the lower edge of the specimen to the uppermost point of the char area. . . . By applying a given weight, (varied according

to the weight of the fabric), to one of the lower corners by means of a hook, while supporting the other lower corner with a lifting motion, a tear is produced through the char area into the good portion of the fabric
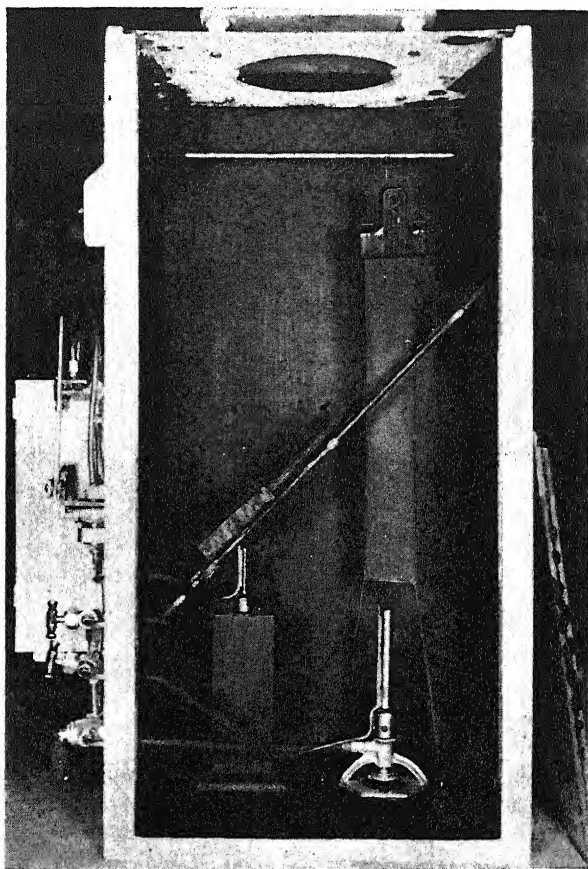
FIGURE 3. Front view of cabinet showing method of attaching fabric to be tested.

which is strong enough to support the weight ... usually accepting a mid-point in any scorched area as the upper limit of char length has given reproducible results.

"The accepted criteria for effective flame resistance of a fabric measured by the vertical flame test method are less than 2 seconds after-flaming, less than 4 seconds afterglow, and a maximum char length of 2.5 to 5.5

inches, depending on the weight of fabric under test, with the higher char lengths allowable for the lighter fabrics."

For other tests applied to flameproofed textiles the reader is referred to the excellent article mentioned above.

POTENTIAL MARKET FOR FLAMEPROOFED TEXTILES

Barnard[2], after reviewing the necessary qualities of flameproofed textiles from the consumer's standpoint, discussed the possible market for such textiles. A survey was made of the large textile mills and key men responsible for the fabrication of various types of finished textiles were asked

TABLE 2. POTENTIAL MARKET FOR FIRE-RETARDANT FABRICS

Type of Woven Product	Total Annual Market	Proportion on Which Fire Retardant Desired	Potential Annual Market
	(Lbs of Cloth)	(%)	(Lbs of Cloth)
Brushed napped and pile fabric	6,900,000	50	3,450,000
Lace curtains	12,000,000	75	9,000,000
Other curtains	30,000,000	50	15,000,000
Sheer goods			
Cotton	36,000,000	75	27,000,000
Rayon	9,000,000	75	6,750,000
Work clothing	270,000,000	5	13,500,000
Chenille bedspreads		0	
Chenille robes	7,700,000	75	5,000,000
Bed linens	160,000,000	2	3,200,000
Upholstery	84,000,000	25	21,000,000
Seat cover cloth	10,000,000	25	2,500,000
Total	625,000,000		106,400,000

what proportion of their market would be interested in fire-resistant finishes. Knowing the total quantities of cotton employed in the fabrication of textiles, he was able to make fairly accurate estimates of the proportion of the various types of manufactured goods that it was deemed desirable to flameproof, providing the cost was but little more than that of other finishes.

These estimates are given in Table 2 in terms of total woven fabrics marketed annually, the percentage that it would be desirable to flameproof and the actual quantity of cloth in pounds that might be so treated.

Assuming that 10 per cent of the weight of the textile was added as a fire-retardant agent, and one-half of this amount was ammonium phosphate, then the annual potential consumption of this salt for flameproofing textile would be 5,320,000 lb or 2,660 short tons. Any appreciable increase

in the cost of the treated goods, however, unquestionably would result in a big reduction in the consumers' demand for flameproofed materials.

FIRE-RESISTANT WOOD

Since the ratio of surface to volume in most wood used for construction purposes is relatively small, the chances of sudden conflagations due to ignition of wood is much less than in the case of textiles. Nevertheless there is ample proof of the highly combustible nature of timber, and fires once started in wooden buildings are difficult to control.

The treatment of wood with flame retardants therefore is extremely important, particularly where it is likely to be highly heated or exposed to sparks from other sources.

Fire retardants for timber may be divided into two broad groups: (1) those which merely protect the surface consisting of coatings of incombustible mineral pigments; and (2) those which are forced into the fiber and permeate an appreciable distance beneath the surface.

Phosphate compounds are used to only a limited extent in fire-retardant products of group (1) since thin coatings of mineral pigments are often more effective and readily applied.

In group (2), however, where the wood is actually impregnated with the flameproofing agent, the salts of phosphoric acid play a highly important role.

Some of the patented products for flameproofing wood are claimed to have both fire retardant and insecticidal properties and thus serve a dual purpose.

A. Gordon[1] describes so-called improved impregnating solutions for the preservation and flameproofing of wood. The inventor claims that the various materials used react to form products which do not leach away, but retain their insecticidal and fire retardant properties under weathering conditions. Mixtures of ammonium phosphate and either zinc or copper sulfate dissolved in aqueous ammonia are two types of solutions used. According to the inventor the products resulting from the reactions are zinc ammonium phosphate ($ZnNH_4PO_4$) and copper ammonium phosphate ($CuNH_4PO_4$) respectively. Both of these are insoluble compounds yet possess fireproofing properties and are toxic to organisms that normally attack wood. The composition of a mixture that is said to embody these two desirable characteristics is as follows:

	(%)
Basic copper carbonate ($CuCO$—$Cu(OH)_2$)	10
Basic zinc carbonate ($ZnCO_3$—$Zn(OH)_2$)	10
Copper ammonium phosphate ($CuNH_4PO_4$)	30
Zinc ammonium-phosphate ($ZnNH_4PO_4$)	30
Zinc borate (ZnB_4O_7)	10
Copper borate (CuB_4O_7)	10

These various compounds in the proportions given above are dissolved in aqueous ammonia and as the ammonia evaporates, insoluble products are precipitated on the surface, as well as in the pores of the wood.

In general the chemicals used for impregnating wood are water-soluble compounds and their solutions are forced into the fibrous structure by a process similar to that used in creosoting timber. This is the only way that fairly adequate flameproofing can be attained. Tests indicate that maximum protection is afforded when wood is impregnated with a solution containing from 12 to 15 per cent of the salt (usually $NH_4H_2PO_4$). The procedure may be briefly described as follows:

The planks or beams (separated by slats) are placed in a steel cylinder (which is then closed), and treated with steam under a pressure of about 25 psi for an hour or more. Any condensed steam is drained off and vacuum is then applied which serves to draw off any moisture as well as air from the pores of the wood permitting the entrance of the fire retardant. The vacuum treatment, however, should not be prolonged as it is desirable to maintain an elevated temperature when the wood is impregnated.

After evacuation the cylinder is completely filled with the impregnating solution which is forced into the pores of the wood by applying an air pressure of 100 to 200 psi depending on the density of the wood being treated.

Flameproofed timber impregnated with soluble salts is usually kiln dried and the product should be stored under cover to protect it from the leaching action of rain water. It is advantageous to use a wood preservative as well as, a flameproofing agent. Zinc chloride in low concentrations is an effective wood preservative.

Although great progress has been made in the flameproofing of textiles, wood and other organic products, further research is highly desirable. A list of U. S. patents dealing with flameproofing processes and products is given in Table 32 of the Appendix.

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29. Miscellaneous Industrial Uses of Phosphoric Acid and Its Derivatives

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The increase in the consumption of phosphate rock during the past twenty years is due not only to the greater demand to meet needs already established, but to the development of new uses for certain manufactured phosphate products[50]. Some of these products and their applications which are discussed in this chapter no doubt will assume far greater importance within the next decade as we recognize more fully how their physical and chemical properties can be advantageously utilized in our industrial economy.

PHOSPHATES IN FERMENTATION PROCESSES AND YEAST CULTURE MEDIA

The processes of fermentation and putrefaction are chemical phenomena which were recognized from earliest times, but their causes remained unknown or unproven until the middle and latter part of the nineteenth century[7, 11, 13, 47, 49, 61]. It was the classical work of Pasteur[61] which definitely established the origin and functions of yeast and convinced the scientific world that fermentation changes were due to specific organisms which produced them in the exercise of their vital functions.

Yeasts are found in nature wherever sugar is present. They occur in various foodstuffs, particularly on the surface of fruit. There are a great many varieties of yeast. Guilliermond and Tanner[29] recognized 18 species.

The genus *Saccharomyces*, however, includes most of those having industrial importance[71].

Just as in the case of animals and the higher types of plant life, phosphorus in the form of orthophosphate plays an essential role in the growth and propagation of yeast and hence is an important constituent of yeast culture media.

While yeast consists chiefly of carbon, hydrogen, oxygen and nitrogen, its mineral content is quite appreciable and the proportions of the various

inorganic ingredients (including phosphates) in a culture medium best suited for the propagation of yeast are the same as those present in the yeast by analysis. In the following analysis (Table 1), reported by Mitscherlich[55], it will be seen that P_2O_5 is the predominating mineral constituent of the ash of the yeast plant. Potash, magnesia and sulfur, however, are also indispensable to the life of yeasts.

As far back as 1860 Pasteur produced a crop of yeast in a liquid medium containing only comparatively simple substances of known composition, such as sugar, ammonium tartrate and a mineral phosphate.

Wroblewski[92] observed that the presence of sodium phosphate increased the fermentation of yeast juice, and Buchner, who also noted the same phenomenon, attributed it to the alkalinity of this phosphate compound.

It is now generally recognized that for rapid decomposition of sugar solutions by fermentation, the presence of a phosphate is highly important

TABLE 1. ANALYSIS OF THE ASH OF YEAST (PER CENT)

Ingredient	Upper Fermentation Yeast	Lower Fermentation Yeast
Potash (K_2O)	38.8	28.3
Lime (CaO)	1.0	4.3
Magnesia (MgO)	6.0	8.1
Phosphoric acid (P_2O_5)	53.9	59.4
Silica (SiO_2)	trace	

if not essential. This phosphate is not only in the yeast juice but is a constituent part of the cell, as shown in Table 1.

Harden[31] states that phosphorus takes a very active part in fermentation and goes through a remarkable cycle of changes. The decomposition of the sugar is accompanied by the formation of a complex hexosephosphate from which the phosphate is split off and again rendered available by means of a special enzyme termed hexophosphatase.

Action of Phosphates in Fermenting Mixtures

When a suitable quantity of a soluble phosphate is added to a fermenting solution of a sugar and yeast juice the rate of fermentation rapidly increases. The speed of the reaction is sometimes as much as 20 times that at which it normally proceeds. This increase in the rate of fermentation continues for a while and then gradually falls to a point approximately equal to the original rate.

Harden and Young[32], after careful experimentation, found that during this period of enhanced fermentation the amount of carbon dioxide and alcohol produced exceed that formed in the absence of phosphate by a

quantity exactly equivalent to the phosphate added in the ratio of CO_2 or $C_2H_5OH:Na_2HPO_4$. It is not within the scope of the present work to give in detail the manner in which these experiments were conducted, but the results obtained indicated that definite chemical reactions occur in which both sugar and phosphate are concerned. This conclusion was confirmed by other experiments in which the solutions used were boiled and filtered (after the rate of fermentation had subsided) and it was found that nearly all of the phosphate was in organic combination.

Harden[31] expresses the reaction between glucose and a dibasic phosphate salt as follows:

$$2C_6H_{12}O_6 + 2Na_2HPO_4 \rightarrow 2CO_2 + 2C_2H_5OH + 2H_2O + C_6H_{10}O_4(Na_2PO_4)_2 \quad (1)$$
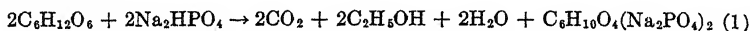
According to the above equation one molecule of sugar is converted into carbon dioxide and alcohol while the other molecule is converted into a hexosephosphate and water.

When alcoholic fermentation ceases, however, there is a marked and rapid increase in the quantity of free or mineral phosphate, since the hexosephosphate undergoes hydrolysis:

$$C_6H_{10}O_4(Na_2PO_4)_2 + 2H_2O \rightarrow C_6H_{12}O_6 + 2Na_2HPO_4 \quad (2)$$
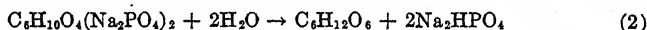
In other words, reversion takes place and glucose and water are again produced. Since the quantity of glucose (or other sugar) thus formed is equivalent only to the mineral phosphate in the solution the reaction cannot again proceed according to equation (1) until further quantities of sugar are added.

If an excess of sugar is present the decomposition of the hexosephosphate (as alcoholic fermentation slackens) gives free mineral phosphate to react with further quantities of glucose but the reaction then proceeds at only a slow or normal rate.

Harden and Young[33] found that by renewing the supply of mineral phosphate (in sugar solutions) as fast as it was converted into hexosephosphate, a high rate of fermentation could be maintained for a considerable period of time.

With few exceptions, all of the yeasts isolated up to the present grow well in artificial media containing inorganic phosphate salts. In Table 2, compiled from data presented by Guilliermond and Tanner[29], some of the common culture media recommended by various authorities are given.

In Table 2 potassium phosphate is the chief carrier of phosphoric acid specified, but disodium phosphate and mono- and dicalcium phosphates are also used. In recent years ammonium phosphate has grown in favor as an ingredient of yeast culture media. This compound furnishes both the P_2O_5 and nitrogen required in the growth and propagation of the yeast cells. Harris *et al.*[34], in a study of the production of yeast from wood-sugar

solutions, found that such solutions contained very few of the requirements for yeast production except the sugar. By adding nitrogen, potash and phosphate salts, however, excellent yields of food yeast were obtained. The optimum nutrient requirements for yeast growth per 100 lbs of sugar in such solutions were 3.4 lbs of nitrogen in the form of urea, 0.65 lbs of K_2O as potassium chloride and 1.6 lbs of P_2O_5 in the form of diammonium phosphate.

A number of patents have been issued in which ammonium phosphate

TABLE 2. COMMON YEAST CULTURE MEDIA CONTAINING INORGANIC SALTS OF ORTHOPHOSPHORIC ACID

Authority	Quantities of Ingredients (G)								
	Peptone	Maltose	Sugar	Asparagin	Magnesium sulfate	Ammonium sulfate	Potassium phosphate	Calcium phosphate	Distilled water
Hansen's medium No. 1	1	5			0.2		0.3		100
Hansen's medium No. 2	1	5			0.5		0.3		100
Mayer's culture medium			15.0		5.0	0.75	5.0	0.5	1000
Laurent's medium			any sugar		0.1	4.71	0.75		1000
Haydruck's medium			100	2.5	17.0		50.0[a]		2000
Colin's solution			20		1.0	2.0[b]	2.0[c]	0.1	200

[a] Potassium acid phosphate (KH_2PO_4).
[b] Ammonium tartrate instead of ammonium sulfate.
[c] Dicalcium phosphate ($CaHPO_4$).

is mentioned as the chief carrier of nitrogen and phosphoric acid in yeast culture processes[12].

No figures are available showing the consumption of phosphate salts in yeast culture. However, the yeast requirements of bakers, brewers and the manufacturers of alcoholic beverages and industrial alcohol are enormous, and the annual consumption of phosphate salts by such industries runs into substantial tonnages.

THE USE OF PHOSPHORIC ACID IN BEVERAGES

With few exceptions, all manufactured beverages or soft drinks contain a small percentage of acid as one of their constituents. Without the addition of an acid, most beverages, particularly those made up with natural or artificial fruit flavors, lack that quality of sharpness which the consumer finds so palatable.

The acids which have been suggested, or are actually being used to impart the desired acidity of sourness to soft drinks, fall into two general classes.

(1) Organic acids such as acetic, citric, tartaric and lactic, all of which are present or formed in food products.

(2) Inorganic or mineral acids such as sulfuric, hydrochloric and phosphoric, all of which are produced on a large scale from inorganic materials.

The term acidity in a chemical sense ordinarily means the neutralizing strength of an acid in terms of a standard alkali solution or the quantity of acid hydrogen present. This, however, is not a true measure of the strength of an acid since the activity of the acid hydrogen varies in different types of acid.

Even though acids have the same concentration, they have a different acid intensity. The most accurate and generally recognized method of measuring the intensity of an acid solution is by the determination of its hydrogen ion concentration (pH) numerically expressed and recorded either by chemical indicators or electrical instruments. The pH of an acid however may be altered by materials which have a tendency to disguise or buffer its intensity. Such substances as sugar, flavors, dissolved salts and other normal ingredients of beverages have such an effect. Soft drinks usually have a pH value ranging between 2 and 4.

Hale and Medbery[30] give the pH values of solutions containing the same amount (by weight) of several of the acids used in soft drinks (Table 3).

From a study of the figures in Table 3, it is obvious that phosphoric acid per unit of weight has a higher acidity than any of the organic acids listed. Acidity, as understood by the manufacturer and bottler of soft drinks, is the degree of sourness (determined by taste) imparted to a beverage by equivalent quantities of acid hydrogen furnished in the form of the acids enumerated above. He is interested particularly in obtaining this desired acidity in the cheapest possible form, provided the acid is pure, digestible and does not detract in any way from the wholesomeness of his product.

In Table 4, originally prepared by Skinner and Sale[72], but modified to conform to present quoted prices, the relative costs of so-called sourness in the form of various organic and inorganic acids used in the manufacture of soft drinks are given.

In column 1 are given the types of acid and the strength of the commercial articles offered on the market. In column 2 are given the pounds of these commercial grades used in 100 gallons of a 1/100 normal acid solution, which is approximately the acidity of the average modern soft drink. In column 3 the relative sourness of such dilute standard acid solutions is given—this degree of sourness being determined by taste. In column

4 are given the weights in pounds of the various acids (commercial grades) which must be added to 100 gallons of water or solution to give equal sourness to a beverage. Finally, in the last 2 columns the cost of this acidity or sourness (at current prices) per 100 gallons and per ½ pint bottle is given.

TABLE 3. SOLUTIONS CONTAINING 70 GRAINS PER GALLON (0.120% ACIDITY) CALCULATED AS CITRIC ACID

Acid	pH	Relative Acidity of Solutions[1]
Citric acid in water	3.20	100
Lactic acid in water	3.05	150
Tartaric acid in water	2.75	450
Phosphoric acid in water	2.68	520

[1] Considering citric acid as unity.

TABLE 4. RELATIVE COST OF SOURNESS IN THE FORM OF VARIOUS ACIDS

Name and Commercial Grade of Acid	Lb of Acid per 100 Gals of N/100 Solution[1]	Relative Sourness of N/100 Solution	Lb of Acid per 100 Gals of Solution of Equal Sourness[2]	Current Prices of Acid per Lb (cents)	Cost of Sourness per 100 Gals of Beverage[3] (cents)	Cost of Sourness per ½ Pint of Beverage (cents)
Acetic acid (56%)	0.894	70	1.276	7.0	8.93	0.0054
Lactic acid (40%)	1.878	100	1.878	10.0	18.78	0.0108
Citric acid (91%)	0.587	100	1.587	27.0	42.85	0.0259
Tartaric acid (99.5%)	0.629	100	0.629	18.0	11.32	0.0069
Phosphoric acid (50%)	0.818	120	0.681	4.0	2.72	0.0017
Sulphuric acid (95%)	0.430	200	0.215	7.0	1.51	0.0009
Hydrochloric acid (37%)	0.823	200	0.411	8.0	3.29	0.0020

[1] Bottled soda of the ginger ale type has an acidity and sourness approximately equal to N/100 solution of citric tartaric or lactic acid. The solutions compared in this column are of equal acidity but not of equal sourness.

[2] The degree of sourness of these solutions is approximately the same as the sourness of bottled soda of the acid type (N/100 solution of citric acid).

[3] According to quotations in *Oil, Paint and Drug Reporter*, Dec. 26, 1949.

It will be noted that acid solutions of equal normality (having the same acid hydrogen content) differ very materially in sourness; the inorganic acids have a much more pronounced acid taste. The cheapest sources of this sourness were found to be sulfuric and phosphoric acids with hydrochloric, acetic, tartaric, lactic and citric acid, following in the order named. The cost of this same degree of acidity in the form of the other organic acids is from four to eight times greater than in the form of phosphoric acid.

The use of the organic acids enumerated above is approved by the U. S. Department of Agriculture, since they are naturally present or formed in food products to which the human digestive tract is accustomed. Therefore, according to Skinner and Sale[72] the presence of these acids in beverages "is quite proper and advisable."

However, of the three inorganic acids mentioned, only phosphoric acid is generally accepted as a wholesome ingredient of soft drinks. The use of sulfuric and hydrochloric acids in food products, according to the authorities cited above, "is questionable to say the least, being considered very undesirable by many."

Phosphoric acid has been employed in the preparation of so-called phosphate beverages such as orange, lemon and cherry phosphates. In recent years, however, this acid has been used chiefly as the acid constituent of beverages of the cola type.

The increased use of phosphoric acid is due not only to its relatively low cost but to the fact that salts or phosphoric acid have certain recognized medicinal value. Moreover, compounds of phosphorus play an important role in the human diet (see Chapter 2), and it is argued that acidity furnished in the form of orthophosphoric acid is certainly not deleterious and probably beneficial to health. No accurate figures are available showing the quantity of phosphoric acid consumed in beverages, but it is unquestionably very appreciable.

According to figures furnished by the American Bottlers of Carbonated Beverages the total quantity of acid of all types used in 1948 amounted to approximately eight million lbs, or 4,000 tons. About 61.6 per cent of these beverages are of the cola type, and if we assume that only 30 per cent of the total acid used was phosphoric we have an annual consumption of 1,200 tons.

Small percentages of phosphoric acid were formerly used to impart acid flavor and tartness to jams and jellies. This use, however, has been discontinued.

Needless to say, however, acid used for food purposes and in carbonated beverages must be free from such deleterious substances as arsenic fluorine and the salts of copper lead, etc. The phosphoric acid produced through the medium of the electric furnace is largely used for food-grade products.

PHOSPHORIC ACID AS A CATALYST AND OIL REFINING AGENT

In addition to their main function of supplying gasoline and other fuels, petroleum and petroleum gases are sources of a multiplicity of organic chemical products that have wide industrial applications.

The breaking down and building up of these hydrocarbon products into other compounds are effected by heat, pressure, chemical treatment, and

by the aid of certain catalysts among which phosphoric acid appears to be playing an increasingly important role.

In 1936 Malishev[52] found that phosphorus pentoxide (P_2O_5) exercised a refining action on vapor phase cracked petroleum distillates and yielded products having a pronounced increase in octane number. Later (1938) Ipatieff and Corson[40] showed that when a stabilized untreated cracked naphtha was contacted in the vapor phase with a so-called solid phosphoric acid catalyst (prepared from a mixture of concentrated H_3PO_4 and diatomaceous earth), the combined effect of the catalyst and distillation improved the color and quality of the product. Compared to a clay used under similar conditions the phosphoric acid catalyst was over ten times more efficient.

Processes whereby the nature and composition of hydrocarbons are altered through the medium of a phosphoric acid catalyst may be grouped under three broad headings: (1) dehydrogenation; (2) polymerization; and (3) alkylation.

Dehydrogenation, as the term implies, is the removal of hydrogen from hydrocarbon molecules. Formerly dehydrogenation was brought about mainly by the decomposition or cracking of petroleum products at very highly elevated temperatures and pressures[4, 43]. With the development of catalysts, however, it was found that the desired results could be accomplished more efficiently and at lower temperatures. A characteristic dehydrogenation reaction is the production of ethylene from ethane as shown below:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
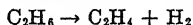
Polymerization is directly opposed to the cracking of petroleum products since its purpose is to build up rather than to break down the hydrocarbon compounds. Heavier molecules are thus produced and gases converted into liquids and liquids into solids. By the use of phosphoric acid catalysts both the temperatures and pressure ordinarily required for such reactions can be materially reduced. The following is a characteristic example of polymerization:

$$\begin{array}{ccccc}
\text{H H} & & \text{H H H H} & & \text{H H H H H H} \\
\overset{\cdot\cdot}{C}\overset{\cdot\cdot}{:}\overset{\cdot\cdot}{C} & + & \text{H}\cdot\overset{\cdot}{C}\cdot\overset{\cdot}{C}\cdot\overset{\cdot}{C}\overset{\cdot\cdot}{:}\overset{\cdot\cdot}{C} & \rightarrow & \overset{\cdot\cdot}{C}\overset{\cdot\cdot}{:}\overset{\cdot}{C}\cdot\overset{\cdot}{C}\cdot\overset{\cdot}{C}\cdot\overset{\cdot}{C}\cdot\text{H} \\
\text{H H} & & \text{H H \quad H} & & \text{H \quad H H H}
\end{array}$$
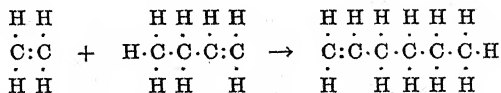
Alkylation is the reaction of dissimilar hydrocarbons, including some olefin, to form a heavier saturated hydrocarbon. Alkylation reactions are favored by high pressures, but can be carried out at reasonably low temperatures in the presence of a catalyst. This process is employed in the manufacture of high-octane motor fuel. A characteristic alkylation re-

action is the conversion of a mixture of propene and benzene into cumene (a high octane blending stock) according to the following equation:

$$C_6H_6 + C_3H_6 \rightarrow C_9H_{12}$$

Phosphoric acid absorbed on kieselguhr is an excellent catalyst for this purpose and its life is very satisfactory[41].

Whereas, orthophosphoric acid is a highly reactive polymerization catalyst, it tends to lose water when heated above 450°F, forming relatively inactive metaphosphoric acid:

$$H_3PO_4 + \text{heat} \rightarrow HPO_3 + H_2O$$
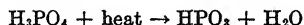
In order to prevent or suppress the dehydration of the phosphoric acid molecule at high temperatures, 2 to 10 per cent of water is introduced as steam into the olefin-feed stock. However, excessive amounts of water may cause the formation of alcohols, increase corrosion and disintegrate the granular catalyst.

The so-called solid phosphoric acid catalysts consist of concentrated phosphoric acid absorbed in a porous inactive granular body such as kieselguhr, alumina, magnesia or a mixture of materials that have been calcined at 180 to 250°C[41, 57].

In the production of poly gasoline the equipment required consists essentially of a heater and two or more catalyst chambers, either of the heat-exchanger type with the catalyst packed inside of tubes, or a plain chamber provided with several spiders for introducing inert gas[3]. The temperature of the heater outlet ranges from 300 to 400°F and the maximum reactor temperature is not over 450°F.

A pressure of about 500 psi is advantageous since it reduces the volume of the gases handled, increases the rate of reaction and facilitates condensation of the products.

According to Nelson[58], as much as 160 gallons of polymer gasoline have been produced per pound of catalyst in recent reactor-type plants operating under a pressure of 900 psig.

At such high efficiency, the catalyst may be discarded after it is spent, but when lower pressures are employed (150 to 200 psig) the yields are much less and hence it pays to regenerate the catalyst. This is done by passing air (at 650°F) over or through the spent catalyst at such a rate that the temperature of the body does not exceed 950°F. The metaphosphoric acid thus formed is then reconverted into orthophosphoric acid by passing steam into the chamber and maintaining it at a temperature of about 500°F for a period of 10 to 15 hours.

Nelson[58] states that the presence of as little as 0.002 mole per cent of oxygen in the gaseous feed reacts to form varnish-like products, which greatly reduce the life of a phosphoric acid catalyst. He also says that

small amounts of ammonia adversely affect the efficiency of such a catalyst. In addition, sulfur is highly injurious to phosphoric acid catalysts since it forms undersirable mercaptans. Feeds for catalytic processes should contain less than 10 grains of hydrogen sulfide per 100 cubic feet.

When operating at temperatures above 500°F, water must be added continously to the gaseous feed; at temperatures below 300°F water must be eliminated.

The copper pyrophosphate (CuP_2O_7) catalytic process as described by Van Winkle[82] is somewhat similar to the phosphoric acid catalytic method. The patent literature describes a number of bodies containing the acid phosphates of alkali earth metals and complex compounds of boron halide and phosphoric acid.

No recent figures are available showing the consumption of phosphoric acid and its compounds as catalytic and refining agents, but it was reported that the petroleum refineries consumed the following quantities in 1941[16]:

	(lbs)
Phosphoric acid	1,300,000
Sodium phosphates	2,225,000
Tricresyl phosphate	696,200
Potassium phosphate	101,000
Sodium metaphosphate	644,000

The demand has increased substantially during the past 10 years and it appears safe to assume that the annual consumption of phosphates in the United States (in terms of phosphoric acid), for processing and refining petroleum products is in excess of 3,000 tons.

PHOSPHATES IN DRILLING FLUIDS

During the past 30 years the use of drilling muds or fluids has been a major factor in the development of deep-seated deposits of oil and gas. Certain phosphate compounds perform essential functions in these fluid suspensions and large quantities are used annually for this purpose.

According to Stern[76] the deepest well in the world 30 years ago was only about 6,000 feet, and in 1930 a 10,000 foot well was considered the ultimate goal. Since the general adoption of drilling mud techniques wells 10,000 feet deep are not uncommon, and depths over 20,000 feet have been attained.

Few industrial mineral products have to meet as many specifications or perform as many functions as a drilling mud. The selection of the raw materials required and their proper blending have been problems on which much time and study have been spent[20, 24, 35, 65]. The basic principle in the use of drilling muds is to pump (under pressure) down to the base of the drill hole an aqueous suspension of clay, heavy minerals and modifying

chemicals, of suitable density, viscosity and well developed colloidal properties; and to circulate this fluid continually after the drill cuttings have been screened or settled out.

The following are some of the functions that drilling mud must perform:

(1) Act as a lubricant and cooling medium for the drill stem and bit, (bottom hole temp. normal gradient—1°F for each 60 ft of depth), protecting them against abrasion and corrosion.

(2) Remove the drill cuttings in suspension as fast as they are produced.

(3) Consolidate the loose formations often met in drilling operations and form an impervious layer or cake on the walls of the drill hole thus checking cave-ins and intrusions of water and brine.

(4) Provide adequate hydrostatic pressure by virtue of adding finely ground heavy minerals thus increasing its density, thereby preventing the blowing out of oil or gas before drilling operations are completed.

(5) Form a gel when allowed to stand and thus hold the drill cuttings in suspension if drilling operations are temporarily suspended.

(6) Release the drill cuttings on agitation so they may be separated by screening or settling and permit the recirculation of the fluid.

Van Dyke[3] says that the ingredients of drilling fluid should be considered tools which have taken much of the guess work out of the use of drilling muds. Some of the more important materials suspended and dissolved in water to form drilling muds and the properties they impart to this product are given in Table 5.

Although certain phosphate chemicals have other direct and indirect effects, their main function is to reduce the viscosity of drilling muds without lowering their density, thus making it feasible to circulate these heavy aqueous suspensions which otherwise could not be readily handled. A secondary, but important effect of reduced viscosity, is the release of high pressure gas that becomes entrapped in the drilling mud..

The salts of orthophosphoric acid do not lower the viscosity of drilling mud since they act as flocculating agents, but pyro-, meta-, and tetraphosphates, which are formed by dehydrating the normal orthophosphates, have the property of deflocculating and dispersing colloidal suspensions of clay, thereby rendering them more fluid and easily pumped.

In aqueous solutions, these complex dehydrated phosphates eventually take up water into their molecular structure and are again converted into orthophosphates. However this change takes place rather slowly and in the meantime they serve as highly efficient deflocculents.

Partridge *et al.*[60] studied these complex phosphates, but only in the last 10 to 12 years have their valuable properties been fully recognized and extensively utilized in the preparation of drilling fluids.

TABLE 5. DRILLING MUD INGREDIENTS, THEIR FUNCTIONS AND EFFECTS

Class of Material	Ingredients and Composition	Primary Function	Effect on Drilling Mud
Inerts	Ordinary native clays Finely divided minerals	To add bulk without appreciably affecting density.	Increase body of fluid and aid suspension of drill cuttings.
Weighting materials	Barite (barium sulfate) Celestite (strontium) Hematite (iron oxide) Galena (lead sulfide)	To increase density of drilling mud to as much as 150 lbs. per cu. ft. without excessive viscosity.	Prevent blow-outs by virtue of their weight.
Thixotropic colloids	Kaolin or Bentonite; Colloidal clays	To increase viscosity and gel strength.	Help build up impervious wall and suspend drill cuttings.
Chemical conditioners	Quebracho (Tannin) and other organics Sodium meta silicate Sodium pyrophosphate Sodium metaphosphates Sodium tetraphosphate	To facilitate pumping and re-circulation of fluid and reduce gas cutting.	Cause deflocculation, and reduce viscosity without affecting density, act as lubricants.

The methods of manufacturing the more important of these phosphate compounds are described in Chapter 24.

The two main shortcomings of sodium pyro-, meta- and tetraphosphates are: (1) their gradual conversion into orthophosphates resulting in loss of deflocculating properties; (2) their inability to offset the flocculating properties of salt water or brine which is often encountered in oil drilling operations in Louisiana and the Gulf states.

The type and quantity of chemicals employed will vary according to conditions. Bonnet[9] found that about 0.5 lb of either sodium pyrophosphate or sodium tetraphosphate per barrel (42 gals) of a heavy drilling mud brought about the optimum reduction in viscosity. Whereas, further additions of pyrophosphate appeared to increase their viscosity, an increase in the amount of the sodium tetraphosphate had little effect in either increasing or decreasing viscosity. Bowman[10] states that from his study of certain oil wells in California the amount of sodium pyrophosphate required averaged approximately 1 lb for each foot in depth. For a 10,000 foot well this would mean a consumption of 5 tons.

Since the activity of the oil industry, the character of the formations encountered and the depth of the wells drilled have a profound effect on the demand for phosphates in drilling fluids, there are no accurate figures available.

For a full discussion of drilling muds and the various materials used in making up products to meet specific problems, the reader is referred to the excellent report of Stern[76] on this subject.

Phosphates in Processing of Textiles

Phosphates play an important role in the processing of textiles whether spun from animal, vegetable, synthetic fibers or mixtures of the three. The salts of phosphoric acid most extensively used for this purpose are trisodium and disodium phosphates and sodium hexametaphosphate.

Removal of Grease and Oil from Cotton and Wool

Trisodium phosphate is used in the preparation of cotton and woolen goods for bleaching and dyeing. In cotton goods this salt serves to emulsify the natural wax of raw cotton, increases the detergent action of the so-called boiling-off liquor, dissolves impurities without impairing the strength of the fibers and shortens the boiling time. The addition of 1 to 1½ per cent of trisodium phosphate to the caustic kier boil also acts as a buffer against the powerful action of sodium hydroxide, and results in cleaner, softer goods that are better prepared for the subsequent bleaching and dyeing steps. After the cotton goods have been boiled, they are rinsed free of caustic soda. It has been found advantageous to add a little trisodium

phosphate to the rinse water in order to remove the last traces of saponified oils, fats and waxes from the fibers.

Because of the nature of wool fibers and their tendency to shrink, woolen textiles require very careful treatment. Trisodium phosphate, however, may be used to advantage in preparing wool for dyeing and in the fulling and finishing steps. Before being dyed, woolen goods must be scoured free from dirt and natural grease. A soap solution at a temperature of not more than 100°F is used. By adding a small per cent of trisodium phosphate the detergent effect of such a scouring solution is considerably enhanced without greatly increasing its causticity. According to White[89] this treatment does not injure the wool fiber but renders it softer and fluffier than any other preliminary processing method. Unless soft water is used in washing textiles, insoluble calcium soaps are apt to be deposited in the goods and cause trouble in the subsequent bleaching and dyeing steps. Trotman[80] states that where soft water is not available the addition of sodium hexametaphosphate to a scouring bath will correct the deleterious effect of water of moderate hardness. The reaction involved is represented as follows:

$$Na_4Na_2(PO_3)_6 + Ca^{++} \rightarrow Na_4Ca(PO_3)_6 + 2Na^{++}$$
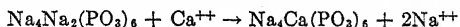
It is said that the addition of sodium hexametaphosphate not only prevents precipitation of calcium soaps but removes any present in the fabric being treated. The pH of the solution should be approximately 8.3.

Dyeing

Disodium phosphate is used as an aid to the dye bath when treating mixtures of fibers (animal, vegetable and synthetic). The function of this salt as a very mild alkali is to retard the absorption of dyestuffs by the animal fibers (silk and wool) and increase the affinity of cotton and rayon for the dye.

The usual procedure is to first add the dyestuff to the solution, followed by an amount of disodium phosphate equal to $\frac{3}{4}$ to 1 per cent of the weight of the goods to be dyed. The goods are then immersed in the bath and the solution boiled for about 20 minutes. Increasing the amount of disodium phosphate decreases the absorption of dye by the animal fibers. Close control over the pH of the solution is important, if not essential, to obtain even dyeing of mixed fibers. This can be readily effected by careful addition of this phosphate salt.

Treatment of Silk

Since silk is the most expensive of all natural fibers, great care must be exercised in its preparation for the market. Phosphates play an important role in the manufacture of silk fabrics. Raw silk consists essentially of a

gum-like material known as sericin, a true silk fiber or fibroin and minor quantities of salts. Its approximate composition is as follows:

	(%)
Silk gum or sericin	22.0 to 25.0
Fabroin or true silk	62.5 to 67.0
Water	10.0 to 11.0
Salts, etc.	1.0 to 1.5

Degumming. The cocoons are first immersed in warm water to soften the gum and loosen the fiber so it may be reeled off in a single thread. The next step is called discharging, stripping, or boiling-off and is really a scouring process designed to remove the sericin or silk glue which causes the fiber to feel coarse or stiff. In the boiling-off process soft or softened water is essential to prevent subsequent trouble in bleaching and dyeing. A warm soap solution containing about 25 per cent of soap to the weight of the silk is used. White[89] claims that a small amount of trisodium phosphate added to the soap solution is preferable to the stronger alkalies since it is more readily washed out and prevents the fiber from becoming harsh.

The raw silk is suspended in a tank of this solution and the temperature gradually increased from 105 to 205°F. Actual boiling should be avoided. After soaking for one-half hour in the first tank, the silk is removed and immersed successively in a second and third batch of a similar solution for the same time and under the same conditions. Finally the boiled-off fiber is washed in hot water containing a little trisodium phosphate to remove the last traces of gum and oil. In this scouring process the silk loses from 20 to 30 per cent in weight, but the product is soft and lustrous and in an excellent condition for the next step in its treatment. The soap solution which becomes heavily charged with the gum-like material (originally a part of the silk fiber) is subsequently utilized in the dyeing process.

Weighting of Silk. After being scoured and washed free of soap, the silk is ready for weighting, which adds to the fiber a quantity of material sometimes more than equal to that lost by the scouring process. Disodium phosphate plays a highly important role in the weighting of silk.

In this process the silk is steeped for 1 hour in a bath of tin tetrachloride, then washed thoroughly and worked for an hour in a bath of disodium phosphate (10°Bé at 150°F), to which a small amount of ammonia is added to neutralize any acidity of the tin-soaked silk. This process was designed not only to restore the weight of the silk fiber lost in the degumming step, but to actually add from 20 to 50 per cent to this original weight. The affinity of silk for tin is such that it will readily take up from 8 to 10 per cent of its weight of this oxide and in some types of goods the weight of the silk is more than doubled. Whereas excessive weighting causes more rapid deterioration of the silk fiber[53], proper tin weighting has a beneficial effect

on both the luster and handling of the silk and if used in connection with phosphates does little harm to the strength, elasticity, and durability of the finished goods.

The discovery of the value of disodium phosphate in the weighting process was a great advance in the art of silk manufacture. Before the advent of phosphates the goods, after being treated with a salt of tin, were immersed in or washed with ammonia water, sodium carbonate, or some other alkali solution. Unless the slight acidity of the tin salt was neutralized, the fiber was unable to be weighted any further by repeated treatments with a tin solution. After neutralization, however, the fiber which acts like a free base is able to take up an additional quantity of the tin salt.

The treatment of the silk with dilute alkali left a precipitate of hydrated tin oxide on the fiber and this free base often proved injurious to the goods when exposed to air and light. By using disodium phosphate the acidity of the tin chloride is neutralized and a phosphate of tin produced, with the result that the durability and strength of the fiber is not greatly diminished, the silk is rendered suitable for dyeing, and the cost of weighting is considerably reduced.

It has subsequently been shown that the use of sodium silicate, in addition to a tin salt and disodium phosphate, makes it possible to increase even further the percentage of tin absorbed by the silk fiber.

PHOSPHORIC ACID AND PHOSPHATES IN PHOTOGRAPHY

Salts of phosphoric acid are used to a limited extent in photographic processes. Di- and trisodium phosphates, monopotassium phosphate and silver phosphate are the salts most generally employed, but monosodium, uranium, manganese, barium and vanadium phosphates have been used in minor quantities though largely in experimental research work.

Free phosphoric acid is employed in the so-called aniline process[22] for reproduction of line subjects. This process is based on the property of bichromate of potash forming with aniline salts dark colored precipitates. The printing paper is coated with a solution of potassium bichromate to which phosphoric acid has been added. After exposure the development of the images or outline is effected by submitting the paper to the action of aniline vapors.

The sensitiveness of silver phosphate to light was discovered by Stromeyer[14] as early as 1830, and this property of the salt was first applied to photography by Dr. Fyfe[91] in 1839, when he made a light-sensitive paper by soaking it in a solution of sodium phosphate, drying it, and then coating one surface with silver nitrate and again immersing it in a solution of sodium phosphate. Silver phosphate in addition to its light sensitiveness is quite insoluble and these two properties make it suitable for use in emul-

sions for printing-out and developing-out papers. Schwartz[67] prepared an emulsion using twice as much disodium phosphate as is necessary to convert the silver nitrate into phosphate, and added potassium chlorate and citric acid with a little chrome alum to harden the film. Such an emulsion is said to be rapid, and easily developed, giving an image of metallic silver having a wide range of tones and the permanence of bromide prints.

Schwartz[67] also described a photographic paper prepared by first applying a protective layer of a phosphate of zinc or an alkaline earth metal. The silver emulsion is then spread over this phosphate layer, the silver salts diffuse into the ground and form insoluble compounds.

Silver phosphate is also used in the Iron Silver Process[69] in conjunction with a light-sensitive organic ferric salt such as ferric oxalate. When the sensitized plate or film is exposed to light, two distinct photochemical reactions take place: The ferric salt is reduced to ferrous salt in proportion to the amount of light received; the silver phosphate which possesses all the properties required for the production of a perfect image is also affected at the same time in proportion to the amount of light received. When these reactions have taken place, the ferrous compound produced will act as a developer for the silver compound in the presence of the alkali salt of the organic acid present, and thus the amount of the developer is automatically proportionate to the amount of exposure which has taken place.

Trisodium phosphate was first suggested by Lumiere[51] as a substitute for alkali metal hydrates or carbonates in alkaline developers. He also proposed the use of trisodium phosphate in the simultaneous development and fixing of photographic images. The following formula is given:

> 1,000 cc of water
> 32 gm of sodium sulfite
> 40 gm of "Hypo"
> 6 gm of metaquinone
> 100 gm of trisodium phosphate

While a generous exposure is usually necessary, the results of using simultaneous developing and fixing baths are claimed to be not only as good as separate developing and fixing baths, but the danger of overdevelopment is materially reduced.

The use of trisodium or tripotassium phosphates in developers is based on their alkalinity[18]. The disodium or dipotassium salt may be used, however, in conjunction with free alkali, since the actual function of the phosphate ion is that of a buffer, regulating the acidity or alkalinity of the bath. Developers containing trisodium phosphate must be made up either with distilled water or water containing sodium hexametaphosphate[84].

The principal value of alkaline phosphates is in developers intended for use in tropical climates. It is possible to use a high concentration of the

alkaline phosphate and obtain the well-known salt depressing action on the swelling of gelatine, which thus reduces the chances of the emulsion softening or dissolving at higher temperatures.

Disodium or dipotassium phosphate probably finds its most extensive photographic use in gold toning baths for printing-out papers. Gold toning is accomplished by substituting metallic gold for metallic silver in the printed-out image, according to the following reaction:

$$AuCl + Ag \rightarrow Au + AgCl$$
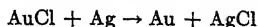
This reaction takes place best under neutral or slightly alkaline conditions and the dialkaline phosphates are often used to furnish the necessary alkalinity[84].

Tricalcium Phosphate and Its Applications

In recent years a number of uses for pure tricalcium phosphate have been developed which render the production of this compound of considerable commercial importance. Precipitated tricalcium phosphate is particularly well suited to serve as a base for neutral or slightly alkaline tooth pastes and powders where a mild abrasive is required which will not scratch the delicate tooth enamel. Its slight basicity also tends to neutralize acidity and correct conditions promoting tooth decay.

When added to food products it furnishes both lime and phosphoric acid and is rendered slowly available by the gastric juices. Tamon[77] recommends the addition of 0.25 to 0.3 gram of tricalcium phosphate and 100 to 200 units of vitamin D per 10 grams of bakery goods to correct calcium deficiency in children.

In certain sections of this country the water contains excessive quantities of soluble fluorine compounds and if consumed regularly for drinking purposes it may cause the teeth to become mottled and discolored. Adler[1] has proposed contacting such water with tricalcium phosphate, which reacts with the fluorine to form insoluble compounds analogous to fluorapatite. Adler claims that the calcium phosphate can be regenerated and its efficiency restored by washing it with a dilute solution of sodium hydroxide.

Practically all table salt contains impurities sufficient to render it somewhat hygroscopic, particularly in certain climates and during seasons when the humidity is high. This hygroscopic property of salt causes it to cake and become so damp at times that it is inconvenient to handle and to distribute uniformly in food products.

It has been found by mixing 1 per cent or more of certain light flocculent precipitated compounds with such salt that the latter loses its caking properties and will flow sufficiently freely to permit its ready distribution in food products.

The probable action of these finely divided insoluble precipitates is to coat the salt grains with a thin film which not only protects them from humidity but acts as a kind of dry lubricant preventing the salt particles from adhering to one another.

The two precipitated compounds which have imparted the desirable free-running property to table salt are magnesium carbonate and tricalcium phosphate. The use of the latter compound has recently grown in favor, it being argued that the presence of small percentages of inorganic phosphates in food products is unobjectionable if not actually desirable.

Moss et al.[55a] compared the relative merits of small additions of tricalcium phosphate, magnesium carbonate and starch as promoters of non-caking and free-running properties to both salt and powdered sugar. Pure tricalcium phosphate (200 to 400 mesh) proved to be a more efficient conditioner for salt than either of the other two materials and did not detract from the luster of the salt grains as did magnesium carbonate.

One per cent of tricalcium phosphate was found to be more effective than 3 per cent of magnesium carbonate and very large percentages of starch in lowering the caking tendency of powdered sugar. It is also said that there is less likelihood that mold will develop in sugar conditioned with tricalcium phosphate than with starch.

Adler[2] also proposed that a basic calcium phosphate, $Ca_3(PO_4)_2 \cdot CaOH$, be mixed with 10 per cent of potassium iodide and added to table salt, claiming that a stabilized free-running iodized product was thus obtained.

Since tricalcium phosphate is generally regarded as the end product, representing the complete neutralization of phosphoric acid by lime, its manufacture would appear off hand to be a relatively simple process*. In actual practice, however, considerable difficulty may be experienced in obtaining a product free from either dicalcium phosphate or hydrated lime unless great care is exercised in its preparation and strict attention given to the various manufacturing details. The general procedure may be briefly described as follows:

An emulsion of milk of lime is first prepared, and to insure the absence of small lumps of burned lime or of undesirable impurities, this emulsion is strained, diluted and mixed with an amount of phosphoric acid slightly less than that theoretically required to produce tricalcium phosphate. The mixture is heated and agitated in large tanks until sufficient time has elapsed for the reaction to be completed. The thin emulsion of tricalcium

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* Some doubt exists as to whether or not tricalcium phosphate is actually the final product of the complete neutralization of H_4PO_4 with CaO. A product is often obtained which more nearly conforms to the formula $Ca_3(PO_4)_2CaO$, moreover, hydroxyapatite $3Ca_3(PO_4)_2CAOH$ has been definitely identified in products formerly regarded as pure tricalcium phosphate.

phosphate is then pumped to a filter press and the bulk of the water eliminated, after which the damp cake is removed and dried at a temperature low enough to prevent the loss of the one molecule of water of crystallization which such tricalcium phosphate contains.

The dried phosphate must be milled to obtain a product of the desired degree of fineness. This operation is relatively simple since it merely consists in breaking up the loose aggregates and is not strictly a grinding process. The material is then put up in barrels or kegs for the market.

The product prepared by the above method will usually contain a little dicalcium phosphate. The conditioning properties of this latter compound are not as good as those of tricalcium phosphate, but the quantity present is relatively small.

No accurate figures are available showing the amount of tricalcium phosphate consumed annually in tooth paste, medicinal preparations, water purification and for conditioning table salt, but it appears conservative to estimate this amount at 10,000,000 lbs or 5,000 tons.

Phosphate Glasses

Phosphoric anhydride (P_2O_5) alone forms a glass but has little or no value for this purpose because of its high solubility[46].

Although various phosphates have been used in the manufacture of glass, aluminum metaphosphate appears to offer more promise as a base than other phosphate compounds. Volume production of pure aluminum phosphate from phosphoric acid and alumina can be readily attained by the larger manufacturers of elemental phosphorus and there should be no difficulty in meeting increasing industrial demands[15]. Many of the true phosphate glasses have a higher P_2O_5 content than the orthophosphates.

The use of phosphates in the manufacture of glass is a radical departure from conventional types of glass made by fusing together lead, silica, lime, soda and potash. Yet the number of possible phosphate glasses exceeds those of the silicates, and hence products possessing a wider variety of physical properties may be obtained. Phosphate glasses not only dissolve substances that are virtually insoluble in silicate glasses, but apparently can tolerate higher proportions of certain impurities without detrimental effects on the physical properties of the final product.

Weyl[85] lists some of the phosphate glasses according to their uses as follows:

(1) Optical glasses having desirable refractive index-dispersion ratios.
(2) Glasses having high ultraviolet transmission.
(3) Fluorescent glasses.
(4) Heat absorbing glasses.
(5) Hydrofluoric acid-resisting glasses.

Optical Glasses

According to Hovestadt[38], the first optical glasses containing phosphates were developed by Schott in an effort to obtain the properties of low-dispersion and high-refraction index. These properties render a glass excellent for achromatizing with the boro-flints in making double objective lenses which are used primarily to eliminate the secondary spectrum.

These earlier phosphate glasses, however, contained high percentages of P_2O_5 and such minor quantities of alumina and boric oxide that they showed poor resistivity to moisture and underwent both physical and chemical changes.

Because of their high transmittance of ultraviolet light and the discovery of the valuable physiological properties of such light, interest was revived in phosphate glasses in 1925. Up to that time only the very costly silica glass met these physical requirements.

In 1926 a new type of ultraviolet transmitting glass was developed consisting largely of calcium phosphate but containing minor quantities of alumina boric oxide and silica. This product, while not altogether satisfactory, was a distinct improvement over the phosphate glasses previously manufactured. Later however, Grimm and Huppert[28] found that aluminum phosphate is not only an efficient vitrifying agent, but yields phosphate glasses having a low coefficient of expansion and a high permeability to ultraviolet light.

The poor chemical resistivity of phosphate optical glasses has been overcome to a considerable extent by increasing their alumina content and adding from 8 to 12 per cent of boron oxide. The workability of such glasses has thus been greatly improved and stable products obtained having a softening point as low as 400°C.

Fluorescent Glasses

Kaufmann and his co-workers[43] reported in 1938 that by the introduction of certain activating oxides fluorescent phosphate glasses of high efficiency could be produced. Since that time other investigators have given considerable study to the manufacture of such glasses activated by small quantities of manganese, uranium, tin, thallium and antimony.

Hooley[37] patented a fluorescent zinc, aluminum phosphate glass activated by cerium oxide that was reported to be quite satisfactory. Rather complete descriptions of fluorescent glasses are given by Weyl[85].

Heat-Absorbing Glasses

Weyl states that "Glasses containing divalent iron are a convenient means for filtering out the near infrared of intensive light sources. These heat filters are slightly bluish green because the absorption band of the

Fe^{2+} in silicate glasses extends into the visible region, lowering the red transmission."

With the development of colored moving pictures, however, it became necessary to produce colorless infrared absorbing filters. E. Berger[5] found that phosphates offered the means of manufacturing such colorless heat-absorbing glasses. These glasses, unlike those consisting of silicates containing 2 to 3 per cent of FeO, do not absorb appreciable amounts of visible light. A number of patents covering glasses of this type have been issued to Pincus[62], Tillyer *et al.*[79], and Tilyer[78]. Tilyer gives the ranges in the composition of such products in Table 6.

Fluorine-Resisting Glasses

One of the outstanding advantages of phosphate glasses is their resistance to attack by hydrofluoric acid. Silicate glasses are rapidly acted upon by

TABLE 6. RANGE IN COMPOSITION OF PHOSPHATE GLASS FOR WINDOW LIGHTS AND LENSES

Ingredient	Range in Composition (%)
Phosphorus pentoxide (P_2O_5)	50 to 75
Silica (SiO_2)	2 to 10
Alumina (Al_2O_3)	8 to 16
Boric oxide (B_2O_3)	1 to 10
Calcium oxide (CaO)	2 to 10

hydrofluoric acid and window panes, gauges and glass faces of instruments exposed to its fumes soon lose their transparency, making them difficult to read. Aluminum phosphate glasses are not appreciably affected by such fumes and their development should be of great value in certain industrial plants such as fertilizer factories and those in which fluorine compounds are manufactured. The advantages of such acid-resisting glasses was recognized by Knaffl[44] as far back as 1884, but it was not till many years later that satisfactory glasses for this purpose were developed.

Opaque and Translucent Glasses

The modern development of electrical illumination and the demand for indirect or diffused lighting has been largely responsible for the growth of the opaque and translucent glass industry. Such materials as bone ash, pure phosphates, guano, magnesium silicates, sodium and calcium fluorides, cryolite, fluosilicates, asbestos, tin oxide, etc., are used as opacifying agents. Alabaster glasses are probably the oldest type of the opaque glasses. They were first made in Bohemia[45] and contained high percentages of silica and small percentages of calcium, but no appreciable amount of phosphoric acid.

In 1743 Kunckel[45] recommended the use of bone ash as an opacifying agent. He used a mixture of 60 lbs of sand, 40 lbs of potassium carbonate and 10 lbs of bone ash. With improvements in the design and operation of glass-making furnaces, better methods and formulas for manufacturing more permanent or durable opaque glasses were sought. In more recent years artificially prepared sodium or calcium phosphates have been used instead of bone ash, since these substances can be prepared very pure and in such a fine state that a more uniform and dependable glass can be obtained.

Rosenhain[64] attributed the opacity of these glasses to small particles of calcium phosphate disseminated throughout the mass, the separation of this compound taking place as the glass cools. According to Weyl[85], however, it seems more likely that the opacity is due to fine crystals of fluorapatite since bone and natural phosphates nearly all contain appreciable amounts of fluorine. Earhart[21] obtained good sanitary ware glazes as opaque as those obtained with oxide of tin by using several phosphate salts.

Opal, opalescent and mother of pearl glasses occupy an important place in the ornamental glass industry. The first iridescent glass appeared about 1870 and since that time the progress has been very marked[70]. The following batch mixture is said to yield one of the most successful mother of pearl glasses.

Sand	100 parts by weight
Potash	45 parts by weight
Red lead	52 parts by weight
Bone ash	8 parts by weight

By adding a small amount of manganese dioxide an excellent imitation of the antique Venetian mother of pearl is obtained with similar translucency and pearly iridescence. Mellor[54] gives the following formula for such glass:

Sand	68	parts by weight
Potash	21	parts by weight
Soda	5	parts by weight
Red lead	5	parts by weight
Saltpeter	1	parts by weight
Borax	1	parts by weight
Calc. spar	4	parts by weight
Bone ash	6–10	parts by weight

These typical formulas illustrate the importance of bone ash or phosphates in the manufacture of ornamental glass.

BONE CHINA

Bone china is a development of the English potters, who obtained their early information indirectly from China. It is the most highly prized chinaware on the market and the most difficult to manufacture. The physical

properties of bone china which appeal so strongly to the connoisseur are its fineness of texture, its translucency and its pearly iridescence.

According to Moore[56], the composition of good bone china may fall within the following range:

	(%)
Bone ash	42 to 32
Feldspar	15 to 19
China clay	33 to 35
Flint	10 to 14

It seems pretty well agreed that the addition of bone ash increases the fluxing action of feldspar[23]. In discussing the constitution of bone china, Weyl[87] concludes that it consists of a glassy phase relatively rich in calcium oxide which accounts for its relatively high refractive index. In addition to minor amounts of quartz and mullite, probably the chief crystalline constituent is apatite. This same authority[88] in a discussion of the "Role of Phosphorus in Bone China" attributes the translucency of bone china to three main factors: (1) degree of vitrification; (2) difference of refractive indices of the glassy and crystalline phase; (3) the absorption of light caused by such impurities as iron compounds.

In preparing a china clay body the materials should be finely ground either separately or after mixing and then subjected to the action of powerful magnets to remove all traces of metallic iron.

The next operation, that of getting the body into the most plastic or workable condition, requires considerable time and attention. Upon grinding Cornish stone or feldspar in water, hydrolysis takes place and china clay and water glass are formed to some extent. In a like manner, the grinding of bone ash in water possibly forms some acid calcium phosphate or even phosphoric acid. As a result of this wet grinding the materials acquire a much greater plasticity. It has been found advantageous to use a bone ash which has retained a large part of its carbon, as it is much more plastic than a hard burned bone ash.

According to Mellor[54], the bone china body cannot be matured or tempered like an ordinary clay body, because the organic matter in the bone ash will begin to putrefy with the development of small gas bubbles. Pug mills cannot be successfully used as the cutting action of the blades tends to make the clay short[8]. Tempering should be accomplished more or less by a kneading action, and the French rolling table is said to more nearly meet these conditions.

In biscuit firing a tremendous contraction takes place up to a certain temperature. Great care must be exercised in this heating operation since excessive temperatures cause expansion and warping of the china and the formation of small bubbles in the ware. These bubbles are caused by the liberation of phosphorus from the bone ash in the body mixture.

On firing in the glost oven and enamel kiln unstable phosphates ranging from the white variety to a blue or bluish-green may oxidize to a brown or spotted brown stain.

Davis[19], in experimenting with precipitated phosphates as substitutes for bone ash, found that such phosphates gave excellent results and that the failures so often blamed on the precipitated phosphate were due to the alkali impurities, thus pure alkali free phosphate gave as good results as bone ash. This suggested the use of Canadian apatites practically alkali free. Four bodies made up using Canadian apatites in lieu of bone ash made excellent ware. Jackson and Holdcroft[42] believe that the substitution of calcium phosphate for bone ash has the same effect on translucency but that the ware has a greater tendency to deform during firing.

At the present time very little bone china is made in this country, but

TABLE 7. COMPOSITION OF TWO MODERN GLAZES CONTAINING BONE ASH

Ingredients	No. 1	No. 2
Sand	100	100
Red lead	60	
Potash	22	30
Bone ash	12	8
Tin oxide	12	
Saltpeter	5	3
Borax	4	
Soda		8
Lime		6
Arsenic		$\frac{1}{2}$

there is no definite reason why the industry should not be more firmly established in the United States as the demand for such ware is very great.

PORCELAIN ENAMELS AND GLAZES

Tricalcium phosphate in the form of bone ash has an extensive use in the china and porcelain glaze industry. According to Collie[17] the Chinese used considerable amounts of phosphate in their fieldspathic glazes for pottery porcelain as early as 960 to 1279 A.D.

Formulas of the more two modern enamel glazes are shown in Table 7.

Fritz[26], however, recommends a batch mix containing a much higher proportion of P_2O_5 to give a brilliant glaze free from the crazing tendency.

White enamel is one of the favorite finishes on steel products but most white enamels will not adhere directly to metal surfaces and it is therefore customary to apply a ground coat first containing materials such as cobalt and nickel that fuse to steel but yield dark-colored enamels. A suitable

mixture is then sprayed upon the ground coat to give white opaque enamel sufficiently thick to mask the dark color of the undercoat.

Whitesell[90] patented a process for manufacturing a white enamel frit which comprised adding forming materials, zirconium silicate and aluminum phosphate to glass. This frit is said to be so effective that a single coat produces a satisfactory opaque white enamel.

In addition to the white or cream colored glasses obtained by the use of aluminum and alkali phosphates, some of the most efficient colors for hard porcelains and glazes are produced by metallic phosphates[36]. Cerium pyrophosphate gives a sulfur yellow color resistant to oxidizing and reducing gases; ferric phosphate produces a chestnut brown; manganese pyrophosphate gives a yellowish brown, and cobalt phosphate and manganese phosphate or dioxide yields a blue black color.

Phosphoric Acid in Dental Cements

Since our natural teeth are composed largely of phosphate of lime it is logical that phosphates should be used in their repair and replacement. Phosphoric acid is widely used in dental cements. Years of careful and painstaking research have been conducted in seeking and in choosing materials to stand up under the deteriorating conditions to which dental cements are exposed. Not only must such cements withstand severe strains and stresses, but they must also be subjected to chemical and bacterial influences which tend to bring about their disintegration.

Good dental cements should have the following properties:

(1) Relatively quick setting and strong adhesive properties.
(2) A coefficient of expansion practically identical with that of the human teeth.
(3) Hardness and a high crushing strength.
(4) The property of being nonporous and resistant to the solvent effect of saliva.
(5) Germicidal properties.

In addition to the above properties, certain types of cements must have a color and translucency simulating the life-like appearance of natural teeth.

According to Souder and Paffenbarger[74] cement restorations comprise approximately 10 per cent of all fillings and if the auxiliary use of such cements are considered (such as bases for metallic fillings, pulp capping, etc.) cements in some form are used in 50 per cent of all dental restorations.

Dental cements have three practical advantages over metallic filling materials: (1) a natural appearance which makes it possible to simulate or match the human teeth; (2) greater speed of manipulation than metals and alloys; and (3) lower heat conductivity.

Whereas, their minor ingredients vary somewhat, phosphate dental cements may be divided into two classes:

(1) Zinc phosphate cements obtained by mixing zinc oxide powder with phosphoric acid.

(2) Silicate cements which are produced by mixing finely ground fused glass-like mixtures with phosphoric acid to form a plastic mass.

A third class of cements containing varying percentages of copper compounds are also produced which have more marked germicidal or antiseptic properties than the two classes mentioned above[73].

Dental cements reach the dentist in the form of a powder and a liquid. These are mixed just prior to use. The powder or solid contains the basic ingredients and the liquid furnishes the acid ingredient. Vogt[83] and Poteschke[63] lay great emphasis on the importance of thoroughly mixing the solid and liquid and upon the consistency of the paste formed, pointing out that the chemical constitution and physical properties of the final product are dependent upon the most intimate contact between the reacting ingredients.

Zinc Phosphate Cements

The main ingredient of the powdered portion of zinc phosphate cements is zinc oxide which has been calcined to render it more slowly reactive with phosphoric acid. These powders may be grouped into 3 classes according to their composition. Class 1 contains almost 100 per cent zinc oxide; class 2 contains zinc and magnesium oxides in the approximate ratios of 9 to 1; class 3 is more complex, since in addition to zinc and magnesium oxides other constituents such as barium sulfate, bismuth oxide, silica, etc., are present in minor quantities. The cement produced from powders of class 2 appear to have superior physical properties[75].

The composition of several samples of these three classes of cement powders is given in Table 8.

The liquid portion of zinc phosphate cements consists of phosphoric acid, but a number of bases are dissolved therein so that the percentage of free acid is substantially reduced. The rate of reaction is slowed down when the liquid and powder are mixed thus preventing premature setting. The water content of the phosphoric acid-phosphate solutions according to Souder and Paffenbarger[74] is within the range of 33 ± 5 per cent.

The composition of typical samples of the phosphoric acid liquid used in zinc phosphate cements is given in Table 9.

The powdered base and acid should be so proportioned that a thick paste is produced and a slight excess of zinc oxide maintained in the mix so that the final product will contain no free phosphoric acid.

The exact nature of the compounds formed by the reaction between the

powder and the liquid are not known, but there is little doubt that zinc phosphates predominate in the final product. As shown by the x-ray diffrac-

TABLE 8. COMPOSITION OF ZINC PHOSPHATE CEMENT POWDERS

Class	Sample	Percentage by Weight					
		ZnO	MgO	SiO₂	R₂O₃	Bi₂O₃	Miscellaneous
1	A	100		0.05	0.05		
	B	99.7		0.10	0.10		CaO 0.10
	C	98.0				1.90	
	D	99.4		0.06	0.10	0.04	
2	E	92.4	7.5	0.10	0.06		CuO 0.10
	F	90.3	8.2	1.40	0.10		
	G	90.2	9.4	0.40	0.07		
	H	89.9	9.1	0.40	0.50		
	I	89.5	9.4	0.30			BaCrO₄ 0.80
3	L	89.1	4.0	1.80	0.50	4.50	
	M	82.2	9.0	3.00	0.90	4.10	CuO 0.80
	N	83.1	7.2	0.10	0.04		BaSO₄ 8.20
	O	84.0	7.2	4.90	1.00		CaF₂ 2.70
	P	74.9	13.0	1.30	2.60		CaO 2.2, B₂O₃ 5.1

TABLE 9. COMPOSITION OF ZINC PHOSPHATE CEMENT LIQUIDS

Class	Sample	PO₄	Al	Zn	Mg	Free H₃PO₄	Total H₃PO₄
1	A	57.4	1.8	10.0		42.8	59.4
	B	55.2	3.4	3.1		41.6	57.1
	C	64.3	2.7			56.8	66.6
	D	57.3	2.1	10.0		41.7	59.3
2	E	64.6	2.7	1.6		55.5	66.9
	F	52.6	2.5	7.1		38.2	54.4
	G	59.9	2.9	2.0		49.4	62.0
	H	59.7	2.1	4.1		50.1	61.8
	I	57.9	2.8		0.30	48.9	59.9
3	L	64.2	2.7	0.9		55.8	66.5
	M	67.2	3.0			58.7	69.6
	N	64.9	2.9			56.6	67.2
	O	54.6	2.3	10.3		37.8	56.5
	P	53.4	2.7			45.5	55.3

tion pattern, these cements have a crystalline structure, the formation of which gives them their setting properties.

The time of setting is most important in the practical application of

phosphate cements[63]. The cement should set relatively slowly at ordinary temperatures but accelerate at somewhat elevated temperatures. In this way the dentist has ample time to mix the ingredients, but the patient will not be inconvenienced in waiting for the cement to harden. Federal specifications call for a setting time of not less than 4 or more than 10 minutes[25].

The compressive strength or hardness of zinc phosphate cements average about 13,000 psi, as against 30,000 lbs for human dentine and about about 100,000 psi for sound tooth enamel.

Zinc phosphate cements are not as durable as metallic fillings. Moreover, while white, they are opaque and lifeless and hence cannot be used for filling or facing anterior teeth.

TABLE 10. COMPOSITION OF SILICATE CEMENT POWDERS

Cement Powder	Percentage by Weight						
	SiO_2	Al_2O_2	CaO	F	Na_2O	P_2O_5	Loss on ignition
SA	47.2	33.1	10.4		8.7		0.7
SB[a]	44.0	21.4	13.6		2.6	7.6	0.8
SC[b]	32.0	29.5	10.5	14.3	9.8	5.8	2.4
SD	39.9	27.7	7.2	15.4	9.0	4.0	0.8
SE[c]	35.1	29.9	9.6	14.2	9.8	5.4	0.1
SF	14.6	15.6	3.9	5.9	3.9	2.1	0.1
SG	37.7	31.7	7.6	12.9	10.0	3.3	0.9

[a] Contained 9.8% BeO and 0.3% NiO

[b] Contained 0.3 Sr

[c] Contained 0.2 Fe_2O_3

Silicate Cements

Silicate cements were developed to meet a long felt need for a material with adhesive and setting properties which would also have a color and translucency approximating that of natural teeth. Whereas, such cements have not been entirely perfected, they have been greatly improved both with regard to their appearance as well as their other physical properties. Paffenbarger[59] estimates that roughly 11,000,000 silicate cement fillings are made annually in the United States, which is rather conclusive evidence of their acceptability.

As in the case of zinc phosphate cements, the production of the silicate cements involves the mixing of a solid and a liquid component. The liquid is a solution of phosphoric acid very similar in composition but somewhat less concentrated than that used in zinc phosphate cements.

The solid or powdered portion of silicate cement is produced by intimately mixing certain proportions of silica, alumina, lime and a flux,

heating this mass to a temperature of 2000 to 2400°F, and finely grinding the resultant glass-like product.

The composition of a number of silicate cement powders is given in Table 10. It will be noted that most of these powders contain appreciable percentages of P_2O_5.

According to Souder and Paffenbarger[75] there is a profound difference between the reactions involved in the setting of silicate and zinc phosphate cements. Whereas, the latter are crystalline products, the former are more in the nature of gels of complex silicates[39].

Most of the silicate cements when properly mixed will set within 3 to 4 minutes at mouth temperature and will eventually obtain a compressive strength of about 24,000 psi. The hardness of phosphate-silicate cements is almost as great as that of dentine, but they are considerably more brittle and are not as resistant to shock as natural teeth. The possibilities of improving the adhesiveness translucency and toughness of such cements still offer a fertile field for research.

The total consumption of phosphoric acid (P_2O_5) for dental purposes probably does not exceed a few tons per year, but the benefits derived from this relatively small quantity used in the repair and restoration of human teeth are immeasurable.

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Appendix

	Symbol	Atomic Weight		Symbol	Atomic Weight
Aluminum	Al	26.97	Molybdenum	Mo	95.95
Antimony	Sb	121.76	Neodymium	Nd	144.27
Argon	A	39.944	Neon	Ne	20.183
Arsenic	As	74.91	Nickel	Ni	58.69
Barium	Ba	137.36	Nitrogen	N	14.008
Beryllium	Be	9.02	Osmium	Os	190.2
Bismuth	Bi	209.00	Oxygen	O	16.0000
Boron	B	10.82	Palladium	Pd	106.7
Bromine	Br	79.916	Phosphorus	P	30.98
Cadmium	Cd	112.41	Platinum	Pt	195.23
Calcium	Ca	40.08	Potassium	K	39.096
Carbon	C	12.010	Praseodymium	Pr	140.92
Cerium	Ce	140.13	Protactinium	Pa	231.
Cesium	Cs	132.91	Radium	Ra	226.05
Chlorine	Cl	35.457	Radon	Rn	222.
Chromium	Cr	52.01	Rhenium	Re	186.31
Cobalt	Co	58.94	Rhodium	Rh	102.91
Columbium	Cb	92.91	Rubidium	Rb	85.48
Copper	Cu	63.54	Ruthenium	Ru	101.7
Dysprosium	Dy	162.46	Samarium	Sm	150.43
Erbium	Er	167.2	Scandium	Sc	45.10
Europium	Eu	152.0	Selenium	Se	78.96
Fluorine	F	19.00	Silicon	Si	28.06
Gadolinium	Gd	156.9	Silver	Ag	107.880
Gallium	Ga	69.72	Sodium	Na	22.997
Germanium	Ge	72.60	Strontium	Sr	87.63
Gold	Au	197.2	Sulfur	S	32.066
Hafnium	Hf	178.6	Tantalum	Ta	180.88
Helium	He	4.003	Tellurium	Te	127.61
Holmium	Ho	164.94	Terbium	Tb	159.2
Hydrogen	H	1.0080	Thallium	Tl	204.39
Indium	In	114.76	Thorium	Th	232.12
Iodine	I	126.92	Thulium	Tm	169.4
Iridium	Ir	193.1	Tin	Sn	118.70
Iron	Fe	55.85	Titanium	Ti	47.90
Krypton	Kr	83.7	Uranium	U	238.07
Lanthanum	La	138.92	Vanadium	V	50.95
Lead	Pb	207.21	Wolfram	W	183.92
Lithium	Li	6.940	Xenon	Xe	131.3
Lutetium	Lu	174.99	Ytterbium	Yb	173.04
Magnesium	Mg	24.32	Yttrium	Y	88.92
Manganese	Mn	54.93	Zinc	Zn	65.38
Mercury	Hg	200.61	Zirconium	Zr	91.22

TABLE 2. WEIGHTS AND MEASURES
A. Linear Measure

12	inches	= 1 foot	10 mm	= 1 centimeter
3	feet	= 1 yard	10 cm	= 1 decimeter
5½	yards	= 1 rod	10 dm	= 1 meter
320	rods	= 1 mile	10 m	= 1 dekameter
1,760	yards	= 1 mile	10 dek-m	= 1 hektometer
5,280	feet	= 1 mile	10 hekt-m	= 1 kilometer

B. Square Measure

144 sq inch	= 1 sq ft	100 sq mm	= 1 sq cm
9 sq ft	= 1 sq yd	100 sq cm	= 1 sq dm
20.25 sq yd	= 1 sq rod	100 sq dm	= 1 sq m
272.25 sq ft	= 1 sq rod	100 sq m	= 1 sq dekameter
160 sq rd	= 1 acre	100 deka m	= 1 hektometer
620 acres	= 1 sq mile	100 sq hekto m	= 1 kilometer

C. Cubic Measure

1,728 cu inch	= 1 cu foot	1000 cu mm	= 1 cu cm
27 cu ft	= 1 cu yd	1000 cu cum	= 1 liter
128 cu ft	= 1 cord	1000 liters	= 1 cu meter

D. Liquid Measure

4 gills	= 1 pint	1000 cu mm	= 1 cc
2 pints	= 1 quart	1000 cu cm	= 1 liter
4 quarts	= 1 gallon	1000 liters	= 1 cu meter
31½ gals	= 1 bbl (U. S.)		
2 bbls	= 1 hogshead		

E. Weight Measures

Avoirdupois		Troy		Metric	
16 drams	= 1 oz	24 grams	= 1 pennywt	10 mg	= 1 centigram
16 oz	= 1 lb	20 pennywt	= 1 oz	10 cgm	= 1 decigram
100 lbs	= 1 cwt	12 oz	= 1 lb	10 decigrm	= 1 gram
20 cwt	= 1 ton			10 gms	= 1 dekagram
				10 dekagms	= 1 hectfogram
				10 hectogms	= 1 kilogram
				1000 kilos	= 1 metric ton

TABLE 3. EQUIVALENT VALUES FOR POWER EXPRESSED IN VARIOUS ENGLISH AND METRIC UNITS

Items	Watt	KW	English HP	Continental HP	Kg M per sec	Ft lb per sec	Kg cal per sec	Btu per sec
1 watt	1.000	0.0010	0.0013	0.0014	0.1020	0.7370	0.0002	0.0010
1 kw	1000.0	1.0000	1.3400	1.3600	102.0	737.000	0.2380	0.9470
1 English hp	746.0	0.7460	1.0000	1.0150	76.0	550.000	0.1780	0.7070
1 Continental hp	735.0	0.7350	0.9850	1.0000	75.0	541.000	0.1750	0.6960
1 kg m per sec	9.81	0.0098	0.0131	0.0133	1.000	7.233	0.0023	0.0093
1 ft lb	1.356	0.0014	0.0018	0.0019	0.1380	1.0000	0.0003	0.0013
1 kcal	4200.0	4.200	5.6100	5.7000	427.000	3090.00	1.0000	3.9680
1 Btu	1055	1.055	0.4150	0.4220	107.600	777.60	0.2520	1.0000

Items	Kw[1] (Hrs)	HP[2] (Hrs)	C to CO[3] (lbs)	C to CO$_2$[4]	Coal[5] (lbs)	Coke[6] (lbs)	Oil[7] (lbs)	Natural[8] Gas (Cu Ft)
1 kw-hr[1]	1.0	1.342	0.762	0.234	0.262	0.282	0.179	2.846
1 hp hrs[2]	0.745	1.00	0.568	0.174	0.196	0.204	0.134	2.121
1 lb C to CO[3]	1.312	1.367	1.0	0.306	0.344	0.360	0.236	3.733
1 lb C to CO$_2$[4]	4.287	5.748	3.269	1.0	1.127	1.176	0.771	12.204
1 lb coal[5]	3.8	5.10	2.901	0.888	1.0	1.044	0.684	10.833
1 lb coke[6]	3.645	4.883	2.779	0.850	0.957	1.00	0.655	10.373
1 lb oil[7]	3.807	7.466	4.241	1.297	1.462	1.526	1.00	15.833
1 cu ft natural gas[8]	0.351	0.432	0.268	0.082	0.092	0.096	0.63	1.00

[1] 1 kw-hr = 3,415 Btu's.
[2] 1 hp hr = 2,545 Btu's.
[3] 1 lb C to CO = 4,480 Btu's.
[4] 1 lb C to CO$_2$ = 14,645 Btu's.
[5] 1 lb coal = 13,000 Btu's.
[6] 1 lb coke = 12,448 Btu's.
[7] 1 lb fuel oil = 19,000 Btu's.
[8] 1 cu ft nat. gas = 1,200 Btu's.

TABLE 5. CHEMICAL CONVERSION FACTORS APPLICABLE TO PHOSPHORUS AND ITS COMPOUNDS

Name	Formula	Mol. Wt.	To Convert To (Multiply by)	
			P 4	P$_2$O$_5$
Aluminum phosphate	AlPO$_4$	122.14	0.254	0.581
Ammon. phosphate, (mono)	NH$_4$H$_2$PO$_4$	115.10	0.269	0.617
(di)	(NH$_4$)$_2$HPO$_4$	132.13	0.235	0.537
(meta)	(NH$_4$)$_4$P$_4$O$_{12}$	388.33	0.312	0.731
Calcium phosphate (mono)	CaH$_4$(PO$_4$)$_2$H$_2$O	252.20	0.242	0.564
(di)	CaHPO$_4$·2H$_2$O	172.15	0.235	0.538
(tri)	Ca$_3$(PO$_4$)$_2$	310.29	0.200	0.458
(meta)	Ca(PO$_3$)$_2$	278.00	0.313	0.718
(pyro)	Ca$_2$P$_2$O$_7$	254.28	0.244	0.559
Magnesium phosphate (di)	MgHPO$_4$·3H$_2$O	174.42	0.178	0.407
(tri)	Mg$_3$(PO$_4$)$_2$·8H$_2$O	407.17	0.152	0.349
(pyro)	Mg$_2$P$_2$O$_7$	222.72	0.279	0.638
Phosphoric acid (ortho)	H$_3$PO$_4$	98.14	0.316	0.725
(meta)	HPO$_3$	80.05	0.388	0.887
(pyro)	H$_4$P$_2$O$_7$	178.11	0.349	0.797
Phosphorus (elemental)	P$_4$	124.16	1.000	2.289
Phosphorus pentoxide	P$_2$O$_5$	142.08	0.437	1.000
Potassium phosphate (mono)	KH$_2$PO$_4$	136.16	0.228	0.522
(di)	K$_2$HPO$_4$	174.25	0.178	0.408
(tri)	K$_3$PO$_4$	212.34	0.146	0.334
(meta)	K$_4$P$_4$O$_{12}$	472.56	0.263	0.601
(pyro)	K$_4$P$_2$O$_7$	330.54	0.188	0.429
Sodium phosphate (mono)	NaH$_2$PO$_4$·H$_2$O	138.07	0.225	0.514
(di)	Na$_2$HPO$_4$·12H$_2$O	358.24	0.089	0.198
(tri)	Na$_3$PO$_4$·12H$_2$O	380.23	0.082	0.187
(meta)	Na$_4$P$_4$O$_{12}$	408.16	0.304	0.696
(pyro)	Na$_4$P$_2$O$_7$·10H$_2$O	446.24	0.139	0.318

TABLE 6. CONVERSION FACTORS (PHYSICAL)

Multiply	By	To Obtain	Multiply	By	To Obtain
Acres	43,560	Square feet	Cubic feet	7.48052	Gallons
Acres	4840	Square yards	Cubic feet	28.32	Liters
			Cubic feet	59.84	Pints (liq)
Atmospheres	76.0	Cms of mercury	Cubic feet	29.92	Quarts (liq)
Atmospheres	29.92	Inches of mercury			
Atmospheres	33.90	Feet of water	Cubic feet/second	0.646317	Million gals/day
Atmospheres	10,333	Kgs/sq meter	Cubic feet/second	448.831	Gallons/min
Atmospheres	14.70	Lbs/sq inch			
			Cubic inches	16.39	Cubic centimeters
Barrels-oil	42	Gallons-oil	Cubic inches	5.787×10^{-4}	Cubic feet
Barrels-cement	376	Pounds-cement	Cubic inches	1.639×10^{-5}	Cubic meters
			Cubic inches	2.143×10^{-5}	Cubic yards
Bags or sacks-cement	94	Pounds-cement	Cubic inches	4.329×10^{-3}	Gallons
			Cubic inches	1.639×10^{-2}	Liters
			Cubic inches	0.03463	Pints (liq)
Board-feet	144 sq in. x 1 in.	Cubic inches	Cubic inches	0.01732	Quarts (liq)
			Cubic meters	35.31	Cubic feet
British Thermal Units	0.2520	Kilogram-calories	Cubic meters	61.023	Cubic inches
			Cubic meters	1.308	Cubic yards
British Thermal Units	777.5	Foot-lbs	Cubic meters	264.2	Gallons
British Thermal Units	3.927×10^{-4}	Horse-power-hrs	Cubic meters	2113	Pints (liq)
			Cubic meters	1057	Quarts (liq)
British Thermal Units	107.5	Kilogram-meters			
			Cubic yards	46,656	Cubic inches
British Thermal Units	2.928×10^{-4}	Kilowatt-hrs	Cubic yards	0.7646	Cubic meters
			Cubic yards	202.0	Gallons
			Cubic yards	764.6	Liters
Btu/min	12.96	Foot-lbs/sec	Cubic yards	1616	Pints (liq)
Btu/min	0.02356	Horse-power	Cubic yards	807.9	Quarts (liq)
Btu/min	0.01757	Kilowatts			
			Degrees (angle)	60	Minutes
Centimeters	0.3937	Inches	Degrees (angle)	0.01745	Radians
			Degrees (angle)	3600	Seconds
Centimtrs of mercury	0.01316	Atmospheres			
			Degrees/sec	0.1667	Revolutions/min
Centimtrs of mercury	0.4461	Feet of water	Degrees/sec	0.002778	Revolutions/sec
Centimtrs of mercury	136.0	Kgs/sq meter	Drams	27.34375	Grains
			Drams	0.0625	Ounces
Centimtrs of mercury	27.85	Lbs/sq ft	Drams	1.771845	Grams
Centimtrs of mercury	0.1934	Lbs/sq inch	Fathoms	6	Feet
			Feet	30.48	Centimeters
Cubic centimeters	3.531×10^{-5}	Cubic feet	Feet	0.3048	Meters
Cubic centimeters	6.102×10^{-2}	Cubic inches			
Cubic centimeters	1.308×10^{-6}	Cubic yards	Feet of water	0.02950	Atmospheres
Cubic centimeters	2.642×10^{-4}	Gallons	Feet of water	0.8826	Inches of mercury
Cubic centimeters	2.113×10^{-3}	Pints (liq)	Feet of water	304.8	Kgs/sq meter
Cubic centimeters	1.057×10^{-3}	Quarts (liq)	Feet of water	62.43	Lbs/sq ft
			Feet of water	0.4335	Lbs/sq inch
Cubic feet	2.832×10^{4}	Cubic cms			
Cubic feet	1728	Cubic inches	Foot-pounds	1.286×10^{-3}	British Thermal Units
Cubic feet	0.02832	Cubic meters			
Cubic feet	0.03704	Cubic yards	Foot-pounds	5.050×10^{-7}	Horse-power-hrs

TABLE 6—*Continued*

Multiply	By	To Obtain	Multiply	By	To Obtain
Foot-pounds	3.241×10^{-4}	Kilogram-calories	Horse-power	10.70	Kg-calories/min
Foot-pounds	0.1383	Kilogram-meters	Horse-power	0.7457	Kilowatts
Foot-pounds	3.766×10^{-7}	Kilowatt-hrs	Horse-power	745.7	Watts
Foot-pounds/sec	7.717×10^{-2}	B. T. Units/min	Horse-power (boiler)	33,479	Btu/hr
Foot-pounds/sec	1.818×10^{-3}	Horse-power	Horse-power (boiler)	9.803	Kilowatts
Foot-pounds/sec	1.945×10^{-2}	Kg-calories/min			
Foot-pounds/sec	1.356×10^{-3}	Kilowatts	Horse-power-hours	2547	British Thermal Units
Gallons	3785	Cubic centimeters	Horse-power-hours	1.98×10^{5}	Foot-lbs
Gallons	0.1337	Cubic feet	Horse-power-hours	641.7	Kilogram-calories
Gallons	231	Cubic inches	Horse-power-hours	2.737×10^{5}	Kilogram-meters
Gallons	3.785×10^{-3}	Cubic meters	Horse-power-hours	0.7457	Kilowatt-hours
Gallons	4.951×10^{-3}	Cubic yards			
Gallons	3.785	Liters	Inches	2.540	Centimeters
Gallons, Imperial	1.20095	U. S. gallons	Inches of mercury	0.03342	Atmospheres
Gallons, U. S.	0.83267	Imperial gallons	Inches of mercury	1.133	Feet of water
			Inches of mercury	345.3	Kgs/sq meter
Gallons water	8.3453	Pounds of water	Inches of mercury	70.73	Lbs/sq ft
			Inches of mercury	0.4912	Lbs/sq inch
Gallons/min	2.228×10^{-3}	Cubic feet/sec			
Gallons/min	0.06308	Liters/sec	Inches of water	0.002458	Atmospheres
Gallons/min	8.0208	Cu ft/hr	Inches of water	0.07355	Inches of mercury
Gallons/min	8.0208	Overflow rate	Inches of water	25.40	Kgs/sq meter
		(ft/hr)	Inches of water	0.5781	Ounces/sq inch
	Area (sq ft)		Inches of water	5.202	Lbs/sq foot
			Inches of water	0.03613	Lbs/sq inch
Grains (troy)	1.0	Grains (avoir)			
Grains (troy)	0.06480	Grams	Kilograms	980.665	Dynes
Grains (troy)	0.04167	Pennyweights	Kilograms	2.205	Lbs
		(troy)	Kilograms	1.102×10^{-3}	Tons (short)
Grains (troy)	2.0833×10^{-3}	Ounces (troy)			
			Kilograms-calories	3.968	British Thermal Unit
Grains/U.S. gal	17.118	Parts/million			
Grains/U.S. gal	142.86	Lbs/million gal	Kilograms-calories	3086	Foot-pounds
Grains/Imp. gal	14.254	Parts/million	Kilograms-calories	1.558×10^{-3}	Horse-power-hrs
			Kilograms-calories	1.162×10^{-3}	Kilowatt-hours
Grams	980.7	Dynes			
Grams	15.43	Grains	Kilogram-calories/	51.43	Foot-pounds/sec
Grams	0.03527	Ounces	min		
Grams	0.03215	Ounces (troy)	Kilogram-calories/	0.09351	Horse-power
Grams	2.205×10^{-3}	Pounds	min		
			Kilogram-calories/	0.06972	Kilowatts
Grams/liter	58.417	Grains/gal	min		
Grams/liter	8.345	Pounds/1000 gal			
Grams/liter	0.062427	Pounds/cubic ft	Kgs/meter	0.6720	Lbs/foot
Grams/liter	1000	Parts/million	Kilometers	3281	Feet
			Kilometers	10^{3}	Meters
Hectares	2.471	Acres	Kilometers	0.6214	Miles
Hectares	1.076×10^{5}	Square feet	Kilometers	1094	Yards
Horse-power	42.44	B. T. Units/min	Kilometers/hr	27.78	Centimeters/sec
Horse-power	33,000	Foot-lbs/min	Kilometers/hr	54.68	Feet/min
Horse-power	550	Foot-lbs/sec	Kilometers/hr	0.9113	Feet/sec
Horse-power	1.014	Horse-power	Kilometers/hr	0.5396	Knots
		(metric)	Kilometers/hr	16.67	Meters/min

TABLE 6—*Continued*

Multiply	By	To Obtain	Multiply	By	To Obtain
Kilometers/hr	0.6214	Miles/hr	Minutes (angle)	2.909×10^{-4}	Radians
Kilowatts	56.92	B. T. Units/min	Ounces	16	Drams
Kilowatts	4.425×10^4	Foot-lbs/min	Ounces	437.5	Grains
Kilowatts	737.6	Foot-lbs/sec	Ounces	0.0625	Pounds
Kilowatts	1.341	Horse-power	Ounces	28.349527	Grams
Kilowatts	14.34	Kg-calories/min	Ounces	0.9115	Ounces (troy)
			Ounces	2.790×10^{-5}	Tons (long)
Kilowatt-hours	3415	British Thermal Units	Ounces	2.835×10^{-5}	Tons (metric)
Kilowatt-hours	2.655×10^6	Foot-lbs	Ounces, troy	480	Grains
Kilowatt-hours	1.341	Horse-power-hrs	Ounces, troy	20	Pennyweights (troy)
Kilowatt-hours	860.5	Kilogram-calories			
Kilowatt-hours	3.671×10^5	Kilogram-meters	Ounces, troy	0.08333	Pounds (troy)
			Ounces, troy	31.103481	Grams
Liters	0.03531	Cubic feet	Ounces, troy	1.09714	Ounces, avoir
Liters	61.02	Cubic inches			
Liters	1.308×10^{-3}	Cubic yards	Ounces (fluid)	1.805	Cubic inches
Liters	0.2642	Gallons	Ounces (fluid)	0.02957	Liters
Liters	2.113	Pints (liq)			
Liters	1.057	Quarts (liq)	Ounces/sq inch	0.0625	Lbs/sq inch
Lumber Width (in.) x Thickness (in.) / 12	Length (ft)	Board Feet	Parts/million	0.0584	Grains/U.S. gal
			Parts/million	0.07016	Grains/Imp. gal
			Parts/million	8.345	Lbs/million gal
Meters	3.281	Feet	Pennyweights (troy)	24	Grains
Meters	39.37	Inches	Pennyweights (troy)	1.55517	Grams
Meters	1.094	Yards	Pennyweights (troy)	0.05	Ounces (troy)
			Pennyweights (troy)	4.1667×10^{-3}	Pounds (troy)
Meters/sec	196.8	Feet/min			
Meters/sec	3.281	Feet/sec	Pounds	256	Drams
Meters/sec	3.6	Kilometers/hr	Pounds	7000	Grains
Meters/sec	0.06	Kilometers/min			
Meters/sec	2.237	Miles/hr	Pounds	453.5924	Grams
Meters/sec	0.03728	Miles/min	Pounds	1.21528	Pounds (troy)
			Pounds	14.5833	Ounces (troy)
Microns	10^{-6}	Meters			
			Pounds (troy)	5760	Grains
Miles	5280	Feet	Pounds (troy)	240	Pennyweights (troy)
Miles	1.609	Kilometers			
Miles	1760	Yards	Pounds (troy)	12	Ounces (troy)
			Pounds (troy)	373.24177	Grams
Miles/hr	44.70	Centimeters/sec	Pounds (troy)	0.822857	Pounds (avoir)
Miles/hr	88	Feet/min	Pounds (troy)	13.1657	Ounces (avoir)
Miles/hr	1.467	Feet/sec	Pounds (troy)	3.6735×10^{-4}	Tons (long)
Miles/hr	1.609	Kilometers/hr	Pounds (troy)	4.1143×10^{-4}	Tons (short)
Miles/hr	0.8684	Knots	Pounds (troy)	3.7324×10^{-4}	Tons (metric)
Miles/hr	26.82	Meters/min			
			Pounds of water	0.01602	Cubic feet
Millimeters	0.03937	Inches	Pounds of water	27.68	Cubic inches
			Pounds of water	0.1198	Gallons
Milligrams/liter	1	Parts/million			
			Pounds of water/min	2.670×10^{-4}	Cubic ft/sec
Million gals/day	1.54723	Cubic ft/sec			
Miner's inches	1.5	Cubic ft/min	Pounds/cubic foot	0.01602	Grams/cubic cm

TABLE 6—*Concluded*

Multiply	By	To Obtain	Multiply	By	To Obtain
Pounds/cubic foot	16.02	Kgs/cubic meter	Square meters	10.76	Square feet
Pounds/cubic foot	5.787×10^{-4}	Lbs/cubic inch	Square meters	3.861×10^{-7}	Square miles
			Square meters	1.196	Square yards
Pounds/foot	1.488	Kgs/meter			
			Square miles	640	Acres
Pounds/sq foot	0.01602	Feet of water	Square miles	27.88×10^6	Square feet
Pounds/sq foot	4.883	Kgs/sq meter	Square miles	2.590	Square kilometers
Pounds/sq foot	6.945×10^{-3}	Pounds/sq inch	Square miles	3.098×10^6	Square yards
Pounds/sq inch	0.06804	Atmospheres	Square millimeters	1.550×10^{-3}	Square inches
Pounds/sq inch	2.307	Feet of water			
Pounds/sq inch	2.036	Inches of mercury	Square yards	2.066×10^{-4}	Acres
Pounds/sq inch	703.1	Kgs/sq meter	Square yards	0.8361	Square meters
			Square yards	3.228×10^{-7}	Square miles
Quadrants (angle)	90	Degrees			
Quadrants (angle)	5400	Minutes	Temp (°C) + 273	1	Abs temp (°C)
Quadrants (angle)	1.571	Radians	Temp (°C) + 17.78	1.8	Temp (°F)
			Temp (°F) + 460	1	Abs temp (°F)
Quarts (dry)	67.20	Cubic inches	Temp (°F) — 32	5/9	Temp (°C)
Quarts (liq)	57.75	Cubic inches	Tons (long)	1016	Kilograms
			Tons (long)	2240	Pounds
Quintal, Argentine	101.28	Pounds	Tons (long)	1.12000	Tons (short)
Quintal, Brazil	129.54	Pounds			
Quintal, Castile, Peru	101.43	Pounds	Tons (metric)	10^3	Kilograms
			Tons (metric)	2205	Pounds
Quintal, Chile	101.41	Pounds			
Quintal, Mexico	101.47	Pounds	Tons (short)	2000	Pounds
Quintal, Metric	220.46	Pounds	Tons (short)	32000	Ounces
			Tons (short)	907.18486	Kilograms
Square centimeters	1.076×10^{-3}	Square feet			
Square centimeters	0.1550	Square inches	Tons (short)	2430.56	Pounds (troy)
			Tons (short)	0.89287	Tons (long)
Square feet	2.296×10^{-5}	Acres	Tons (short)	29166.66	Ounces (troy)
Square feet	929.0	Square centimeters	Tons (short)	0.90718	Tons (metric)
Square feet	0.09290	Square meters	Tons of water/24 hrs	83.333	Pounds water/hr
Square feet	3.587×10^{-8}	Square miles	Tons of water/24 hrs	0.16643	Gallons/min
			Tons of water/24 hrs	1.3349	Cu ft/hr
$\dfrac{1}{\text{Sq ft/gal/min}}$	8.0208	Overflow rate (ft/hr)	Watts	0.05692	B. T. Units/min
			Watts	44.26	Foot-pounds/min
			Watts	0.7376	Foot-pounds/sec
Square inches	6.452	Square centimeters	Watts	1.341×10^{-3}	Horse-power
			Watts	0.01434	Kg-calories/min
Square inches	6.944×10^{-3}	Square feet			
Square inches	645.2	Square millimeters	Watt-hours	3.415	British Thermal Units
			Watt-hours	2655	Foot-pounds
Square kilometers	247.1	Acres	Watt-hours	1.341×10^{-3}	Horse-power-hrs
Square kilometers	10.76×10^6	Square feet	Watt-hours	0.8605	Kilogram-calories
Square kilometers	0.3861	Square miles	Watt-hours	3671	Kilogram-meters
Square kilometers	1.196×10^6	Square yards			
			Yards	91.44	Centimeters
Square meters	2.471×10^{-4}	Acres	Yards	0.9144	Meters

TABLE 7. SULFURIC ACID CONVERSION TABLES

Allowance for Temperature

At 10°Bé 0.029°Bé or 0.00023 Sp. Gr. 1°F
At 20°Bé 0.036°Bé or 0.00034 Sp. Gr. 1°F
At 30°Bé 0.035°Bé or 0.00039 Sp. Gr. 1°F
At 40°Bé 0.031°Bé or 0.00041 Sp. Gr. 1°F
At 50°Bé 0.028°Bé or 0.00045 Sp. Gr. 1°F
At 60°Bé 0.026°Bé or 0.00053 Sp. Gr. 1°F
At 66°Bé 0.024°Bé or 0.00054 Sp. Gr. 1°F

Bé at 60°F	Sp. Gr.	Wt. Lb per Cu Ft	Wt. Lb/Gal	% H_2SO_4	% 66° Acid	Equiv. Lb 66° Acid per Cu Ft	Equiv. Lb 66° Acid per Gal
0.0	1.0000	62.37	8.338	0.00	0.00	0.00	0.000
1.0	1.0069	62.80	8.395	1.02	1.09	0.68	.091
2.0	1.0140	63.24	8.455	2.08	2.23	1.41	.189
3.0	1.0211	63.69	8.515	3.13	3.36	2.14	.286
4.0	1.0284	64.14	8.575	4.21	4.52	2.90	.388
5.0	1.0357	64.60	8.636	5.28	5.67	3.66	.489
6.0	1.0432	65.06	8.697	6.37	6.84	4.45	.595
7.0	1.0507	65.53	8.734	7.45	7.99	5.24	.701
8.0	1.0584	66.01	8.825	8.55	9.17	6.06	.810
9.0	1.0662	66.50	8.890	9.66	10.37	6.89	.921
10.0	1.0741	66.99	8.956	10.77	11.56	7.74	1.035
11.0	1.0821	67.49	9.023	11.89	12.76	8.61	1.151
12.0	1.0902	68.00	9.091	13.01	13.96	9.49	1.269
13.0	1.0985	68.51	9.159	14.13	15.16	10.39	1.389
14.0	1.1069	69.04	9.230	15.25	16.36	11.30	1.511
15.0	1.1154	69.57	9.300	16.38	17.58	12.23	1.635
16.0	1.1240	70.10	9.372	17.53	18.81	13.19	1.763
17.0	1.1328	70.65	9.445	18.71	20.08	14.18	1.896
18.0	1.1417	71.21	9.520	19.89	21.34	15.20	2.032
19.0	1.1508	71.78	9.596	21.07	22.61	16.23	2.170
20.0	1.1600	72.35	9.661	22.25	23.87	17.26	2.306
20.5	1.1647	72.64	9.700	22.84	24.50	17.80	2.377
21.0	1.1694	72.93	9.739	23.43	25.14	18.33	2.448
21.5	1.1741	73.23	9.779	24.02	25.77	18.88	2.521
22.0	1.1798	73.53	9.818	24.61	26.41	19.42	2.593
22.5	1.1836	73.83	9.858	25.21	27.05	19.97	2.667
23.0	1.1885	74.13	9.898	25.81	27.69	20.52	2.741
23.5	1.1934	74.43	9.939	26.42	28.34	21.09	2.817
24.0	1.1983	74.73	9.980	27.03	29.00	21.67	2.894
24.5	1.2033	75.05	10.021	27.65	29.67	22.27	2.974
25.0	1.2083	75.36	10.063	28.28	30.34	22.86	3.053
25.5	1.2134	75.67	10.105	28.90	31.01	23.47	3.135
26.0	1.2185	75.99	10.148	29.53	31.69	24.08	3.216
26.5	1.2236	76.31	10.191	30.16	32.36	24.70	3.299
27.0	1.2288	76.64	10.234	30.79	33.04	25.32	3.381
27.5	1.2340	76.96	10.277	31.42	33.71	25.95	3.465
28.0	1.2393	77.29	10.321	32.05	34.39	26.58	3.549

TABLE 7—*Continued*

Bé at 60°	Sp. Gr.	Wt. Lb per Cu Ft	Wt. Lb/Gal	% H₂SO₄	% 66° Acid	Equiv. Lb 66° Acid per Cu Ft	Equiv. Lb 66° Acid per Gal
28.5	1.2446	77.63	10.366	32.69	35.07	27.23	3.636
29.0	1.2500	77.96	10.410	33.33	35.76	27.88	3.723
29.5	1.2554	78.30	10.456	33.98	36.46	28.55	3.812
30.0	1.2609	78.64	10.501	34.63	37.16	29.22	3.902
30.5	1.2664	78.99	10.547	35.28	37.85	29.90	3.993
31.0	1.2719	79.33	10.593	35.93	38.55	30.58	4.083
31.5	1.2775	79.68	10.640	36.59	39.26	31.29	4.178
32.0	1.2832	80.03	10.687	37.26	39.98	32.00	4.273
32.5	1.2889	80.38	10.734	37.92	40.69	32.71	4.368
33.0	1.2946	80.74	10.782	38.58	41.40	33.43	4.464
33.5	1.3004	81.10	10.830	39.25	42.11	34.14	4.562
34.0	1.3063	81.47	10.879	39.92	42.83	34.89	4.660
34.5	1.3122	81.84	10.929	40.59	43.55	35.64	4.760
35.0	1.3182	82.21	10.978	41.27	44.28	36.40	4.861
35.5	1.3242	82.59	11.029	41.95	45.01	37.17	4.964
36.0	1.3303	82.97	11.079	42.63	45.74	37.95	5.067
36.5	1.3364	83.35	11.130	43.31	46.47	38.74	5.172
37.0	1.3426	83.73	11.181	43.99	47.20	39.52	5.278
37.5	1.3488	84.11	11.233	44.67	47.93	40.32	5.385
38.0	1.3551	84.52	11.286	45.35	48.66	41.13	5.492
38.5	1.3615	84.91	11.339	46.03	49.39	41.95	5.601
39.0	1.3679	85.31	11.392	46.72	50.13	42.77	5.711
39.5	1.3744	85.72	11.447	47.41	50.87	43.61	5.823
40.0	1.3810	86.13	11.501	48.10	51.61	44.45	5.936
40.5	1.3876	86.54	11.556	48.78	52.34	45.30	6.050
41.0	1.3942	86.96	11.611	49.47	53.08	46.16	6.163
41.5	1.4010	87.38	11.668	50.17	53.83	47.04	6.281
42.0	1.4078	87.80	11.724	50.87	54.58	47.92	6.399
42.5	1.4146	88.24	11.782	51.56	55.32	48.82	6.519
43.0	1.4216	88.67	11.839	52.26	56.07	49.72	6.638
43.5	1.4286	89.11	11.898	52.96	56.82	50.64	6.761
44.0	1.4356	89.54	11.956	53.66	57.58	51.56	6.884
44.5	1.4428	89.99	12.016	54.36	58.33	52.49	7.010
45.0	1.4500	90.44	12.076	55.07	59.09	53.42	7.136
45.5	1.4573	90.89	12.137	55.77	59.84	54.39	7.264
46.0	1.4646	91.35	12.198	56.48	60.60	55.36	7.392
46.5	1.4721	91.81	12.260	57.19	61.36	56.35	7.524
47.0	1.4796	92.28	12.322	57.90	62.13	57.33	7.656
47.5	1.4872	92.75	12.386	58.61	62.89	58.33	7.790
48.0	1.4948	93.23	12.449	59.32	63.65	59.34	7.924
48.5	1.5026	93.72	12.514	60.03	64.41	60.37	8.061
49.0	1.5104	94.20	12.579	60.75	65.18	61.40	8.199
49.5	1.5183	94.70	12.645	61.46	65.95	62.46	8.340
50.0	1.5263	95.20	12.711	62.18	66.72	63.52	8.481
50.5	1.5344	95 70	12.779	62.92	67.51	64.62	8.628

TABLE 7—*Continued*

Bé at 60°	Sp. Gr.	Wt. Lb per Cu Ft	Wt. Lb/Gal	% H₂SO₄	% 66° Acid	Equiv. Lb 66° Acid per Cu Ft	Equiv. Lb 66° Acid per Gal
51.0	1.5426	96.21	12.847	63.66	68.31	65.72	8.776
51.5	1.5508	96.72	12.916	64.39	69.10	66.84	8.925
52.0	1.5591	97.24	12.985	65.13	69.89	67.96	9.075
52.5	1.5676	97.76	13.055	65.88	70.69	69.12	9.230
53.0	1.5761	98.30	13.126	66.63	71.50	70.28	9.385
53.5	1.5847	98.84	13.198	67.38	72.30	71.47	9.544
54.0	1.5934	99.38	13.271	68.13	73.11	72.66	9.702
54.5	1.6022	99.93	13.344	68.89	73.92	73.88	9.865
55.0	1.6111	100.48	13.418	69.65	74.74	75.10	10.028
55.5	1.6201	101.04	13.493	70.41	75.55	76.35	10.195
56.0	1.6292	101.61	13.568	71.17	76.37	77.60	10.362
56.5	1.6384	102.18	13.645	71.96	77.23	78.90	10.538
57.0	1.6477	102.76	13.722	72.75	78.07	80.22	10.713
57.5	1.6571	103.36	13.802	73.55	78.93	81.58	10.894
58.0	1.6667	103.95	13.881	74.36	79.79	82.94	11.075
58.5	1.6763	104.55	13.961	75.17	80.66	84.34	11.262
59.0	1.6860	105.16	14.041	75.99	81.54	85.75	11.449
59.5	1.6959	105.78	14.124	76.83	82.44	87.21	11.645
60.0	1.7059	106.40	14.207	77.67	83.35	88.68	11.842
60.5	1.7160	107.03	14.292	78.55	84.29	90.22	12.047
61.0	1.7262	107.66	14.376	79.43	85.23	91.76	12.253
61.5	1.7365	108.31	14.463	80.36	86.23	93.41	12.473
62.0	1.7470	108.96	14.549	81.30	87.24	95.06	12.693
62.5	1.7576	109.62	14.638	82.32	88.33	96.84	12.932
63.0	1.7683	110.28	14.727	83.34	89.43	98.62	13.170
63.5	1.7791	110.97	14.818	84.50	90.67	100.62	13.437
64.0	1.7901	111.65	14.908	85.66	91.92	102.63	13.704
64.5	1.8012	112.35	15.002	87.15	93.52	105.08	14.032
65.0	1.8125	113.05	15.095	88.65	95.13	107.54	14.360
65.5	1.8239	113.76	15.190	90.92	97.56	111.00	14.823
66.0	1.8354	114.47	15.286	93.19	100.00	114.47	15.286

TABLE 8. PHOSPHORIC ACID CONVERSION FACTORS
Phosphoric Acid at 17.5°C

Sp. Gr.	Bé	% P_2O_5	% H_3PO_4	Sp. Gr.	Bé	% P_2O_5	H_3PO_4
1.017	2.3	2.5	3.44	1.223	26.2	25.5	35.13
1.021	2.9	3.0	4.13	1.228	26.7	26.0	35.82
1.025	3.4	3.5	4.82	1.233	27.2	26.5	36.50
1.029	4.0	4.0	5.51	1.239	27.8	27.0	37.19
1.033	4.5	4.5	6.20	1.244	28.3	27.5	37.88
1.037	5.0	5.0	6.89	1.249	28.7	28.0	38.57
1.041	5.5	5.5	7.57	1.255	29.3	28.5	39.26
1.045	6.0	6.0	8.26	1.260	29.7	29.0	39.95
1.049	6.6	6.5	8.95	1.265	30.2	29.5	40.64
1.053	7.2	7.0	9.64	1.271	30.7	30.0	41.33
1.058	7.8	7.5	10.33	1.276	31.2	30.5	42.01
1.062	8.3	8.0	11.02	1.281	31.6	31.0	42.70
1.066	8.8	8.5	11.71	1.287	32.2	31.5	43.39
1.070	9.4	9.0	12.40	1.292	32.6	32.0	44.08
1.074	9.9	9.5	13.09	1.298	33.1	32.5	44.77
1.079	10.5	10.0	13.77	1.303	33.6	33.0	45.46
1.083	11.0	10.5	14.46	1.308	34.0	33,5	46.15
1.087	11.6	11.0	15.15	1.314	34.5	34.0	46.84
1.091	12.0	11.5	15.84	1.319	34.9	34.5	47.52
1.096	12.6	12.0	16.53	1.325	35.4	35.0	48.21
1.100	13.0	12.5	17.22	1.330	35.8	35.5	48.90
1.104	13.5	13.0	17.91	1.336	36.3	36.0	49.59
1.109	14.1	13.5	18.60	1.342	36.8	36.5	50.28
1.113	14.7	14.0	19.28	1.348	37.2	37.0	50.97
1.118	15.2	14.5	19.97	1.354	37.7	37.5	51.66
1.122	15.6	15.0	20.66	1.359	38.1	38.0	52.35
1.126	16.1	15.5	21.35	1.365	38.6	38.5	53.04
1.130	16.5	16.0	22.04	1.371	39.1	39.0	53.72
1.135	17.1	16.5	22.73	1.377	39.6	39.5	54.41
1.140	17.7	17.0	23.42	1.383	39.9	40.0	55.10
1.145	18.3	17.5	24.11	1.389	40.4	40.5	55.79
1.150	18.8	18.0	24.80	1.396	40.9	41.0	56.48
1.155	19.3	18.5	25.48	1.402	41.4	41.5	57.17
1.159	19.7	19.0	26.17	1.409	41.9	42.0	57.86
1.164	20.2	19.5	26.86	1.415	42.3	42.5	58.55
1.169	20.8	20.0	27.55	1.422	42.9	43.0	59.23
1.174	21.3	20.5	28.24	1.428	43.3	43.5	59.92
1.178	21.8	21.0	28.93	1.435	43.8	44.0	60.61
1.183	22.3	21.5	29.62	1.441	44.2	44.5	61.30
1.188	22.8	22.0	30.31	1.448	44.6	45.0	61.99
1.193	23.3	22.5	30.99	1.455	45.1	45.5	62.68
1.198	23.8	23.0	31.68	1.462	45.6	46.0	63.37
1.203	24.3	23.5	32.37	1.469	46.0	46.5	64.06
1.208	24.8	24.0	33.06	1.476	46.5	47.0	64.75
1.213	25.3	24.5	33.75	1.484	47.0	47.5	65.43
1.218	25.8	25.0	34.44	1.491	47.5	48.0	66.12

TABLE 8—*Concluded*

Sp. Gr.	Bé	% P$_2$O$_5$	H$_3$PO$_4$	Sp. Gr.	Bé	% P$_2$O$_5$	H$_3$PO$_4$
1.498	47.9	48.5	66.81	1.653	57.0	58.5	80.59
1.505	48.4	49.0	67.50	1.661	57.5	59.0	81.28
1.513	48.8	49.5	68.19	1.669	57.8	59.5	81.97
1.521	49.5	50.0	68.88	1.677	58.4	60.0	82.65
1.528	49.8	50.5	69.57	1.685	58.7	60.5	83.34
1.536	50.4	51.0	70.26	1.693	59.0	61.0	84.03
1.543	50.7	51.5	70.94	1.701	59.5	61.5	84.72
1.551	51.3	52.0	71.63	1.709	59.9	62.0	85.41
1.559	51.7	52.5	72.32	1.717	60.3	62.5	86.10
1.566	52.2	53.0	73.01	1.725	60.6	63.0	86.79
1.574	52.6	53.5	73.70	1.733	61.0	63.5	87.48
1.581	53.1	54.0	74.39	1.741	61.5	64.0	88.16
1.589	53.5	54.5	75.08	1.750	61.8	64.5	88.85
1.597	54.0	55.0	75.77	1.758	62.1	65.0	89.54
1.605	54.4	55.5	76.45	1.766	62.6	65.5	90.23
1.613	54.8	56.0	77.14	1.775	63.0	66.0	90.92
1.621	55.3	56.5	77.83	1.783	63.4	66.5	91.61
1.629	55.7	57.0	78.52	1.792	63.9	67.0	92.30
1.637	56.2	57.5	79.21	1.800	64.2	67.5	92.99
1.645	56.6	58.0	79.90	1.809	64.5	68.0	93.67

TABLE 9. NITRIC ACID CONVERSION TABLES

Allowance for Temperature

At 10 to 20°Bé—1/30°Bé or 0.00029 Sp. Gr. = 1°F
At 20 to 30°Bé—1/23°Bé or 0.00044 Sp. Gr. = 1°F
At 30 to 40°Bé—1/20°Bé or 0.00060 Sp. Gr. = 1°F
At 40 to 48.5°Bé—1/17°Bé or 0.00084 Sp. Gr. = 1°F

°Bé	Sp. Gr. 60°/60°F	% HNO$_3$	°Bé	Sp. Gr. 60°/60°F	HNO$_3$
10.00	1.0741	12.86	20.00	1.1600	26.24
10.25	1.0761	13.18	20.25	1.1624	26.61
10.50	1.0781	13.49	20.50	1.1647	26.96
10.75	1.0801	13.81	20.75	1.1671	27.33
11.00	1.0821	14.13	21.00	1.1694	27.67
11.25	1.0841	14.44	21.25	1.1718	28.02
11.50	1.0861	14.76	21.50	1.1741	28.36
11.75	1.0881	15.07	21.75	1.1765	28.72
12.00	1.0902	15.41	22.00	1.1789	29.07
12.25	1.0922	15.72	22.25	1.1813	29.43
12.50	1.0943	16.05	22.50	1.1837	29.78
12.75	1.0964	16.39	22.75	1.1861	30.14
13.00	1.0985	16.72	23.00	1.1885	30.49
13.25	1.1006	17.05	23.25	1.1910	30.86
13.50	1.1027	17.38	23.50	1.1934	31.21
13.75	1.1048	17.71	23.75	1.1959	31.58
14.00	1.1069	18.04	24.00	1.1983	31.94
14.25	1.1090	18.37	24.25	1.2008	32.31
14.50	1.1111	18.70	24.50	1.2033	32.68
14.75	1.1132	19.02	24.75	1.2058	33.05
15.00	1.1154	19.36	25.00	1.2083	33.42
15.25	1.1176	19.70	25.25	1.2109	33.80
15.50	1.1197	20.02	25.50	1.2134	34.17
15.75	1.1219	20.36	25.75	1.2160	34.56
16.00	1.1240	20.69	26.00	1.2185	34.94
16.25	1.1262	21.03	26.25	1.2211	35.33
16.50	1.1284	21.36	26.50	1.2236	35.70
16.75	1.1306	21.70	26.75	1.2262	36.09
17.00	1.1328	22.04	27.00	1.2288	36.48
17.25	1.1350	22.38	27.25	1.2314	36.87
17.50	1.1373	22.74	27.50	1.2340	37.26
17.75	1.1395	23.08	27.75	1.2367	37.67
18.00	1.1417	23.42	28.00	1.2393	38.06
18.25	1.1440	23.77	28.25	1.2420	38.46
18.50	1.1462	24.11	28.50	1.2446	38.85
18.75	1.1485	24.47	28.75	1.2473	39.25
19.00	1.1508	24.82	29.00	1.2500	39.66
19.25	1.1531	25.18	29.25	1.2527	40.06
19.50	1.1554	25.53	29.50	1.2554	40.47
19.75	1.1577	25.88	29.75	1.2582	40.89

TABLE 9—*Concluded*

°Bé	Sp. Gr. 60°/60°F	% HNO$_3$	°Bé	Sp. Gr. 60°/60°F	% HNO$_3$
30.00	1.2609	41.30	39.50	1.3744	60.06
30.25	1.2637	41.72	39.75	1.3777	60.71
30.50	1.2664	42.14	40.00	1.3810	61.38
30.75	1.2692	42.58	40.25	1.3843	62.07
31.00	1.2719	43.00	40.50	1.3876	62.77
31.25	1.2747	43.44	40.75	1.3909	63.48
31.50	1.2775	43.89	41.00	1.3942	64.20
31.75	1.2804	44.34	41.25	1.3976	64.93
32.00	1.2832	44.78	41.50	1.4010	65.67
32.25	1.2861	45.24	41.75	1.4044	66.42
32.50	1.2889	45.68	42.00	1.4078	67.18
32.75	1.2918	46.14	42.25	1.4112	67.95
33.00	1.2946	46.58	42.50	1.4146	68.73
33.25	1.2975	47.04	42.75	1.4181	69.52
33.50	1.3004	47.49	43.00	1.4216	70.33
33.75	1.3034	47.95	43.25	1.4251	71.15
34.00	1.3063	48.42	43.50	1.4286	71.98
34.25	1.3093	48.90	43.75	1.4321	72.82
34.50	1.3122	49.35	44.00	1.4356	73.67
34.75	1.3152	49.83	44.25	1.4392	74.53
35.00	1.3182	50.32	44.50	1.4428	75.40
35.25	1.3212	50.81	44.75	1.4464	76.28
35.50	1.3242	51.30	45.00	1.4500	77.17
35.75	1.3273	51.80	45.25	1.4536	78.07
36.00	1.3303	52.30	45.50	1.4573	79.03
36.25	1.3334	52.81	45.75	1.4610	80.04
36.50	1.3364	53.32	46.00	1.4646	81.08
36.75	1.3395	53.84	46.25	1.4684	82.18
37.00	1.3426	54.36	46.50	1.4721	83.33
37.25	1.3457	54.89	46.75	1.4758	84.48
37.50	1.3488	55.43	47.00	1.4796	85.70
37.75	1.3520	55.97	47.25	1.4834	86.98
38.00	1.3551	56.52	47.50	1.4872	88.32
38.25	1.3583	57.08	47.75	1.4910	89.76
38.50	1.3615	57.65	48.00	1.4948	91.35
38.75	1.3647	58.23	48.25	1.4987	93.13
39.00	1.3679	58.82	48.50	1.5026	95.11
39.25	1.3712	59.43			

TABLE 10. HYDROCHLORIC ACID CONVERSION TABLES

Allowance for Temperature

At 10 to 15°Bé—1/40°Bé or 0.0002 Sp. Gr. = 1°F
At 15 to 22°Bé—1/30°Bé or 0.0003 Sp. Gr. = 1°F
At 22 to 25°Bé—1/28°Bé or 0.00035 Sp. Gr. = 1°F

°Bé	Sp. Gr. 60/60°F	% HCl	°Bé	Sp. Gr. 60/60°F	% HCl
1.00	1.0069	1.40	14.25	1.1090	21.68
2.00	1.0140	2.82	14.50	1.1111	22.09
3.00	1.0211	4.25	14.75	1.1132	22.50
4.00	1.0284	5.69	15.00	1.1154	22.92
5.00	1.0357	7.15	15.25	1.1176	23.33
5.25	1.0375	7.52	15.50	1.1197	23.75
5.50	1.0394	7.89	15.75	1.1219	24.16
5.75	1.0413	8.26	16.0	1.1240	24.57
6.00	1.0432	8.64	16.1	1.1248	24.73
6.25	1.0450	9.02	16.2	1.1256	24.90
6.50	1.0469	9.40	16.3	1.1265	25.06
6.75	1.0488	9.78	16.4	1.1274	25.23
7.00	1.0507	10.17	16.5	1.1283	25.39
7.25	1.0526	10.55	16.6	1.1292	25.56
7.50	1.0545	10.94	16.7	1.1301	25.72
7.75	1.0564	11.32	16.8	1.1310	25.89
8.00	1.0584	11.71	16.9	1.1319	26.05
8.25	1.0603	12.09	17.0	1.1328	26.22
8.50	1.0623	12.48	17.1	1.1336	26.39
8.75	1.0642	12.87	17.2	1.1345	26.56
9.00	1.0662	13.26	17.3	1.1354	26.73
9.25	1.0681	13.65	17.4	1.1363	26.90
9.50	1.0701	14.04	17.5	1.1372	27.07
9.75	1.0721	14.43	17.6	1.1381	27.24
10.00	1.0741	14.83	17.7	1.1390	27.41
10.25	1.0761	15.22	17.8	1.1399	27.58
10.50	1.0781	15.62	17.9	1.1408	27.75
10.75	1.0801	16.01	18.0	1.1417	27.92
11.00	1.0821	16.41	18.1	1.1426	28.09
11.25	1.0841	16.81	18.2	1.1435	28.26
11.50	1.0861	17.21	18.3	1.1444	28.44
11.75	1.0881	17.61	18.4	1.1453	28.61
12.00	1.0902	18.01	18.5	1.1462	28.78
12.25	1.0922	18.41	18.6	1.1471	28.95
12.50	1.0943	18.82	18.7	1.1480	29.13
12.75	1.0964	19.22	18.8	1.1489	29.30
13.00	1.0985	19.63	18.9	1.1498	29.48
13.25	1.1006	20.04	19.0	1.1508	29.65
13.50	1.1027	20.45	19.1	1.1517	29.83
13.75	1.1048	20.86	19.2	1.1526	30.00
14.00	1.1069	21.27	19.3	1.1535	30.18

TABLE 10—*Concluded*

°B.	Sp. Gr. 60°/60°F	% HCl	°B.	Sp. Gr. 60°.60°F	% HCl
19.4	1.1544	30.35	22.5	1.1836	36.16
19.5	1.1554	30.53	22.6	1.1846	36.35
19.6	1.1563	30.71	22.7	1.1856	36.54
19.7	1.1572	30.90	22.8	1.1866	36.73
19.8	1.1581	31.08	22.9	1.1875	36.93
19.9	1.1590	31.27	23.0	1.1885	37.14
20.0	1.1600	31.45	23.1	1.1895	37.36
20.1	1.1609	31.64	23.2	1.1904	37.58
20.2	1.1619	31.82	23.3	1.1914	37.80
20.3	1.1628	32.01	23.4	1.1924	38.03
20.4	1.1637	32.19	23.5	1.1934	38.26
20.5	1.1647	32.38	23.6	1.1944	38.49
20.6	1.1656	32.56	23.7	1.1953	38.72
20.7	1.1666	32.75	23.8	1.1963	38.95
20.8	1.1675	32.93	23.9	1.1973	39.18
20.9	1.1684	33.12	24.0	1.1983	39.41
21.0	1.1694	33.31	24.1	1.1993	39.64
21.1	1.1703	33.50	24.2	1.2003	39.86
21.2	1.1713	33.69	24.3	1.2013	40.09
21.3	1.1722	33.88	24.4	1.2023	40.32
21.4	1.1732	34.07	24.5	1.2033	40.55
21.5	1.1741	34.26	24.6	1.2043	40.78
21.6	1.1751	34.45	24.7	1.2053	41.01
21.7	1.1760	34.64	24.8	1.2063	41.24
21.8	1.1770	34.83	24.9	1.2073	41.48
21.9	1.1779	35.02	25.0	1.2083	41.72
22.0	1.1789	35.21	25.1	1.2093	41.99
22.1	1.1798	35.40	25.2	1.2103	42.30
22.2	1.1808	35.59	25.3	1.2114	42.64
22.3	1.1817	35.78	25.4	1.2124	43.01
22.4	1.1827	35.97	25.5	1.2134	43.40

Analysis of Phosphates

A. Guide for Prospectors

Place a small crystal of ammonium molybdate (about ½ the size of a pea) on the surface of rock to be tested. Add a few drops of dilute nitric acid (10 per cent solution). If appreciable quantities of phosphate are present, the crystal and that portion of the rock immediately adjacent thereto will soon be covered with a bright yellow precipitate of ammonium phosphomolybdate. A faint yellow color indicates the presence of very little phosphate and heavy effervescence shows the rock is high in carbonate of lime.

B. Qualitative Test

If the above test indicates that the rock is phosphatic, finely grind a small quantity, and place about 1 g in a 100 cc flask or beaker. Add 25 cc of concentrated nitric acid and boil till red fumes cease to be evolved, filter, wash residue once or twice

with hot water and make up filtrate to approximately 250 cc. Take 25 cc of filtrate, neutralize with ammonia, add a few drops of nitric acid, and then 50 cc of ammonium molybdate solution and stir. A copious yellow precipitate shows the presence of sufficient phosphate to warrant a quantitative analysis of the rock.

OFFICIAL METHODS FOR DETERMINATION OF PHOSPHATES* AND PHOSPHATIC FERTILIZERS

Total Phosphoric Acid

2.7 *Gravimetric Method*

Reagent:

(a) *Molybdate Solution.* Dissolve 100 g of MoO_3 in a mixture of 144 ml of NH_4OH and 271 ml of H_2O. Cool, and pour solution slowly and with constant stirring into a cool mixture of 489 ml of HNO_3 and 1148 ml of H_2O. Keep final mixture in a warm place for several days or until portion heated to 40° deposits no yellow precipitate of NH_4 phosphomolybdate. Decant solution from any sediment and preserve in glass-stoppered vessels.

(b) *Ammonium Nitrate Solution.* Dissolve 100 g of phosphate-free NH_4NO_3 in H_2O and dilute to 1 liter.

(c) *Magnesia Mixture.* (1) Dissolve 11 g of MgO in HCl $(1 + 4)$, avoiding an excess of the acid, add a little MgO in excess, boil a few minutes to precipitate Fe, Al, and P_2O_5, and filter. To filtrate add 140 g of NH_4Cl and 130.5 ml of NH_4OH and dilute to 1 liter. Or, (2) dissolve 55 g of crystallized $MgCl_2 \cdot 6H_2O$ in H_2O, add 140 g of NH_4Cl and 130.5 ml of NH_4OH, and dilute to 1 liter. Or, (3) dissolve 55 g of crystallized $MgCl_2 \cdot 6H_2O$ in H_2O, and 140 g of NH_4Cl, and dilute to 870 ml. Add NH_4OH to each required portion of solution just before using, at rate of 15 ml per 100 ml of solution.

(d) *Ammonium Hydroxide Solution for Washing.* $(1 + 9)$ Should contain not less than 2.5 per cent of NH_3 by weight.

(e) *Magnesium Nitrate Solution.* Dissolve 150 g of MgO in HNO_3 $(1 + 1)$, avoiding an excess acid, add a little MgO in excess, boil, filter from excess of MgO, Fe_2O_3 etc., and dilute to 1 liter.

2.8 *Preparation of Solution*

Treat 2 g of sample by one of methods given below, cool solution, dilute to 200 ml, mix, and pour on dry filter.

(a) Dissolve in 30 ml of HNO_3, and 3 to 5 ml of HCl and boil until organic matter is destroyed. (Suitable for materials containing small quantity of organic matter.)

(b) Dissolve in 15 to 30 ml of HCl and 3 to 10 ml of HNO_3. (Recommended for fertilizers containing much Fe or Al phosphate and for basic slag.)

(c) Evaporate with 5 ml of the $Mg(NO_3)_2$ solution, ignite, and dissolve in HCl. (Suitable for organic material like cottonseed meal alone or in mixtures.)

(d) Boil with 20 to 30 ml of H_2SO_4 in 200-ml flask, adding 2 to 4 g of $NaNO_3$ or KNO_3 at beginning of digestion and small quantity after solution has become nearly colorless, or adding the nitrate in small portions from time to time. When solution is colorless, add 150 ml of H_2O and boil for a few minutes. (Generally applicable to materials or mixtures containing large quantities of organic matter. With cottonseed meals and materials of like nature it is best to add first ±5 ml of HNO_3 and then the H_2SO_4.) Before adding the nitrate, allow to digest, at a gentle heat if necessary, until violence of reaction is over.

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2.9 *Determination*

Pipet aliquot of prepared solution corresponding to 0.25 g, or 1 g, into a 250-ml beaker, add NH₄OH in slight excess, and barely dissolve precipitate formed with a few drops of HNO₃, stirring vigorously. If HCl or H₂SO₄ has been used as solvent, add ±15 g of crystalline NH₄NO₃ or a solution containing that quantity. To hot solution add 70 ml of the molybdate solution for every decigram of P_2O_5 present. Digest at ±65° for 1 hour, and determine whether or not P_2O_5 has been completely precipitated by adding more molybdate solution to clear supernatant liquid. Filter, and wash with cold H₂O or preferably with the NH₄NO₃ solution. Dissolve precipitate on filter with NH₄OH (1 + 1) and hot H₂O and wash into beaker to volume of not more than 100 ml. Neutralize with HCl, using litmus paper or bromothymol blue as indicator, cool, and from buret add slowly (±1 drop/second), stirring vigorously, 15 ml of the magnesia mixture for each decigram of P_2O_5 present. After 15 minutes add 12 ml of NH₄OH. Let stand until supernatant liquid is clear (usually 2 hours), filter, wash precipitate with NH₄OH (1 + 9) until the washings are practically free from chlorides, dry, burn at low heat, and ignite to constant weight, preferably in electric furnace, at 950 to 1000°, cool in desiccator, and weigh as $Mg_2P_2O_7$. Report as percentage of P_2O_5.

With basic slag dehydrate aliquot (20 ml) of prepared solution by evaporating to dryness on steam or hot water bath. Treat with 5 ml of HCl and 25 ml of hot H₂O, digest in order to complete the solution, and filter off SiO₂. Proceed as above. Before precipitating with magnesia mixture, add 5 ml of 5 per cent Na acetate solution.

2.10 *Volumetric Method (4)*

(a) *Molybdate Solution.* To 100 ml of molybdate solution 2.7 (a), add 5 ml of HNO₃. Filter this solution immediately before using.

(b) *Standard Sodium or Potassium Hydroxide Solution.* Dilute 323.81 ml of N alkali, free from carbonates, to 1 liter; 100 ml of the solution should neutralize 32.38 ml of N acid; 1 ml = 1 mg or 1 per cent of P_2O_5 on basis of 0.1 g of substance. For basic slag standardize against a standard phosphate material of about same composition as sample under examination. (Burets in constant use are likely to become so corroded as to increase their capacity and therefore should be tested at least once a year.)

(c) *Standard Acid Solution.* Prepare solution of HCl or of HNO₃, corresponding to strength of (b), or ½ of this strength, and standardize by titration against that solution, using the penolphthalein indicator.

(d) *Phenolphthalein Indicator.* Dissolve 1 g of phenolphthalein in 100 ml of alcohol.

2.11 *Preparation of Solution*

Treat 2 g of sample as directed under 2.8 (a), (b), (c), or (d), preferably (a) when these acids are suitable solvents, and dilute to 200 ml with H₂O.

2.12 *Determination*

(a) For percentages up to 5 use an aliquot corresponding to 0.4 g of substance; for percentages between 5 and 20 use an aliquot corresponding to 0.2 g of substance; and for percentages above 20 use an aliquot corresponding to 0.1 g of substance. Add 5 to 10 ml of HNO₃, depending on method of solution (or equivalent in NH₄NO₃); add NH₄OH until precipitate that forms dissolved only slowly on stirring vigorously, dilute to 75 to 100 ml, and adjust to temperature of 25 to 30°. If the sample is of such nature that it will not give a precipitate with NH₄OH as a test of neutralization, make

solution slightly alkaline to litmus with NH_4OH and then slightly acid with dilute HNO_3. For percentages below 5, add 20 to 25 ml of the freshly filtered molybdate solution; for percentages between 5 and 20, add 30 to 35 ml of the molybdate solution, and for percentages greater than 20, add sufficient molybdate solution to insure complete precipitation. Place solution in shaking or stirring apparatus and shake or stir 30 minutes at room temperature, decant at once through filter, and wash precipitate twice by decantation with 25 to 30 ml portions of H_2O, agitating thoroughly and allowing to settle. Transfer precipitate to filter and wash with cold H_2O until filtrate from 2 fillings of filter yields pink color upon addition of phenolphthalien and 1 drop of standard alkali. Transfer precipite and filter to the beaker or precipitating vessel, dissolve precipitate in small excess of standard alkali, add few drops of phenolphthalein indicator, and titrate with the standard acid.

(b) Not applicable to superphosphate and other fertilizers that contain sulfates

(5) Proceed as directed under (a) to point where solution is diluted to 75 to 100 ml. Heat in water bath to 45 to 50°, add the molybdate solution at rate of 75 ml for each decigram of P_2O_5 present, and allow mixture to remain in bath 30 minutes, stirring occasionally. Decant at once through filter, wash, and titrate as directed under (a).

2.13 *Water-Soluble Phosphoric Acid*

Gravimetric Method. Place 1 g of sample on 9-cm filter and wash with successive small portions of H_2O until filtrate measures $\pm$ 250 ml. Allow each portion of wash H_2O to pass through filter before adding more and use suction if the washing cannot otherwise be completed within 1 hour. If filtrate is turbid, add 1 to 2 ml of HNO_3. Dilute to convenient volume, mix well, and proceed as directed under 2.9.

2.14 *Volumetric Method*

Treat sample as directed under 2.13. To aliquot of solution corresponding to 0.1, 0.2, or 0.4 g, add 10 ml of HNO_3, nearly neutralize with NH_4OH, dilute to 60 ml, and proceed as directed under 2.12.

2.15 *Citrate-Insoluble Phosphoric Acid*

Reagents:

Ammonium Citrate Solution. (6) Should have a sp gr of 1.09 at 20° and pH of 7.0 as determined by electrometric method with hydrogen electrode or by colorimetric method with phenol red. When using colorimetric method proceed as follows:

Dissolve 370 g of crystallized citric acid in 1500 ml of H_2O and nearly neutralize by adding 345 ml of NH_4OH (28 to 29 per cent NH_3). If concentration of NH_3 is less than 28 per cent, add correspondingly larger volume and dissolve the citric acid in correspondingly smaller volume of H_2O. Cool, and make exactly neutral as follows:

Transfer 10 ml of the citrate solution to standard test tube of a hydrogen-ion comparator set with color standards and add 0.5 ml of 0.02 per cent phenol red solution or sufficient volume to give same concentration of indicator as used in color standards. Add from graduated pipet a few drops of NH_4OH (1 + 7) mix, compare color by use of comparator with that of color standards of same indicator, add more NH_4OH if necessary, and repeat test until color matches that of color standard corresponding to pH of 7.0. If the NH_4OH added is in excess of that required to give pH of 7.0 repeat test, using smaller quantity of NH_4OH. From quantity of NH_4OH required to produce in sample a color that exactly matches, standard, calculate quantity of NH_4OH required to neutralize solution. Add this quantity of NH_4OH and check pH of solution by repeating test as before with the addition of a small quantity of NH_4OH or

of a citric solution as may be required. When color matches, dilute solution, if necessary, to density of 1.09 at 20°. (Volume will be ±2 liters.) Keep in tightly stoppered bottles and check pH from time to time.

Phenol red is recommended in place of bromothymol blue as salt effect due to presence of NH_4 citrate solution gives pH reading with latter indicator that is ±0.20 unit too high. When bromothothymol blue is used, subtract 0.20 from observed reading. The other reagents and solutions are described under 2.7 and 2.10.

2.16 *Determination* (7)

(a) *Acidulated Samples*. After washing out water-soluble P_2O_5, 2.13, transfer filter and residue, within period not to exceed an hour, to 250-ml flask containing 100 ml of the NH_4 citrate solution previously heated to 65° in water bath. Close flask tightly with a smooth rubber stopper and shake vigorously until filter paper is reduced to a pulp, relieving pressure by momentarily removing stopper. Loosely stopper flask to prevent evaporation and return it to the bath. Maintain contents of flask at exactly 65°, keeping level of H_2O in bath above that of the citrate solution in the flask. Shake flask every 5 minutes. At expiration of exactly 1 hour from time filter and residue were introduced, remove flask from bath and immediately filter contents as rapidly as possible through Whatman filter paper No. 5 or other paper of equal speed and retentiveness. (It is recommended that filtration be made with suction and use of Büchner funnel or ordinary funnel with Pt or other cone.) Wash with H_2O at 65° until volume of filtrate is +350 ml allowing time for thorough draining before adding new portions of H_2O. If sample gives a cloudy filtrate, wash with a 5 per cent NH_4NO_3 solution. Determine P_2O_5 in citrate-insoluble residue by one of following methods: (1) Dry filter and contents, transfer to crucible, ignite until all organic matter is destroyed, and digest with 10 to 15 ml of HCl until all phosphate is dissolved; (2) transfer wet filter with contents to 200-ml flask, add 30 to 25 ml of HNO_3 and 5 to 10 ml of HCl, and boil until all phosphate is dissolved; or (3) treat filter and contents as directed under 2.8 (c) or (d). Dilute solution to 200 ml, mix well, filter through a dry filter, and proceed as directed 2.9 or 2.12.

(b) *Non-Acidulated Samples other than Basic Slag*. Place 1 g of sample on 9 cm filter paper. Without previously washing with H_2O, proceed as directed under (a) and determine P_2O_5 as directed under 2.9 or 2.12. If substance contains much animal matter (bone, fish, etc.), dissolve residue insoluble in NH_4 citrate by one of processes described under 2.8 (c) or (d).

2.17 *Citrate-Soluble and Available Phosphoric Acid*

Subtract sum of water-soluble and citrate-insoluble P_2O_5 from total to obtain the citrate-soluble P_2O_5. Subtract citrate-insoluble P_2O_5 from total to obtain chemically available P_2O_5 in acidulated samples, dicalcium phosphate, precipitated bone phosphate and precipitated bone.

2.18 *Citric Acid-Soluble Phsophoric Acid in Basic Slag* (8)

Gravimetric Method

Preparation of Solution. Weigh 5 g of prepared slag, 2.2, into a 500-ml cylindrical shaking flask (Wagner) containing 5 ml of alcohol. (Neck of flask should be at least 22 mm wide, and graduation marks at least 8 cm below mouth.) Make up to mark with 2 per cent citric acid solution at 17.5°. Fit flask with rubber stopper and place at once in a rotary apparatus, shaking flask 30 minutes at 30 to 40 rpm. Filter immediately on dry filter and analyze solution at once.

2.19 *Determination*

To 50 ml of the clear filtrate in the beaker add 100 ml of molybdate solution, 2.7 (a), and place beaker in water bath, when temperature of contents reaches 65°, remove beaker and cool to room temperature. Filter, and wash yellow precipitate of NH_4 phosphomolybdate 4 or 5 times with 1 per cent HNO_3. Dissolve precipitate in 100 ml of cold 2 per cent NH_4OH, and nearly neutralize with HCl. Add to solution dropwise, with continuous stirring, 15 ml of magnesia mixture, 2.7 (c) and proceed as directed under (2.9).

2.20 *Volumetric Method*

In an aliquot of the clear solution, 2.18, determine P_2O_5 as directed under (2.12).

TABLE 11. U. S. PATENTS ON WASHING, SCREENING AND DRYING OF
PHOSPHATE ROCK

Patent No.	Date	Patentee
86,289	Jan. 26, 1869	Duvall, A.
86,574	Feb. 2, 1869	Ottolengin, A. M.
114,693	May 9, 1871	Lewis, G. T.
335,673	Feb. 9, 1886	Bacon, E. V.
971,830	Oct. 4, 1910	Coates, L. R.
1,014,254	Jan. 9, 1912 .	Pratt, N. P.
1,014,255	do	do
1,124,442	Jan. 12, 1915	Hoover, F. K., *et al.*
1,129,407	Feb. 23, 1915	Lay, W. F.
1,192,545	July 25, 1916	Memminger, C. G.
1,266,730	May 21, 1918	Webster, H. A.
1,393,840	Oct. 18, 1921	Shoeld, M.
1,429,407	Feb. 23, 1921	Lay, W. F.
1,434,596	Nov. 7, 1922	Dorr, J. V. N.
1,434,597	do	do
1,447,610	Mar. 6, 1923	Allen, C.
1,447,970	Mar. 13, 1923	Dull, R. W.
1,448,181	do	Babka, J. J.
1,453,571	May 1, 1923	Stevenson, E. P.
1,457,810	June 5, 1923	Alwart, P. J.
1,458,111	do	Sturtevant, T. J.
1,467,355	Sept. 11, 1923	Christensen, N. C.
1,468,844	Sept. 25, 1923	Trott, R. S.
1,473,341	Nov. 6, 1923	Gibson, W. A., *et al.*
1,479,834	Jan. 8, 1924	Reynolds, M. P.
1,485,568	Mar. 4, 1924	Ruprecht, C. C.
1,534,180	Apr. 21, 1925	Komarek, G.
1,535,120	Apr. 28, 1925	Kanowitz, S. B., *et al.*
1,546,946	July 21, 1925	Singleton, Gray
1,556,250	Oct. 6, 1925	Rigg, G., *et al.*
1,567,335	Dec. 29, 1925	Scrive, P.
1,641,337	Sept. 6, 1927	Komarek, G.
1,663,881	Mar. 27, 1928	Gibson, W. A., *et al.*
1,669,820	May 15, 1928	Harned, G. T.
1,671,765	May 29, 1928	do
1,741,063	Dec. 24, 1929	Mason, A. J.

TABLE 11—*Continued*

Patent No.	Date	Patentee
1,780,915	Nov. 11, 1930	Hardinge, H.
1,781,526	do	Reynolds, M. P.
1,786,399	Dec. 23, 1930	Krider, G. E.
1,810,416	June 16, 1931	Harty, W. A., *et al.*
1,810,794	do	Shuey, P. McG., *et al.*
1,888,910	Nov. 22, 1932	Gooch, S. D.
1,901,221	Mar. 14, 1933	Bullwinkel, J. T.
1,996,547	Apr. 2, 1935	Mason, A. J.
2,125,663	Aug. 2, 1938	Wuensch, C. E.
2,127,307	Aug. 16, 1938	Oppen, E.
2,139,789	Dec. 13, 1938	Wuensch, C. E.
2,139,823	do	Hayworth, M. E.
2,148,067	Feb. 21, 1939	Fuller, C. M.
2,148,068	do	do
2,150,226	Mar. 14, 1939	Kennedy, J. E.
2,155,748	Apr. 25, 1939	Pool, W. O., *et al.*
2,156,168	do	Thomas, B. D.
2,156,483	May 2, 1939	Sallee, W. I.
2,161,476	June 6, 1939	Seja, A. H.
2,164,052	June 27, 1939	Bullwinkel, J. T.
2,184,226	Dec. 19, 1939	Opie, W. L.
2,191,743	Feb. 27, 1940	Scott, C. H.
2,191,744	do	do
2,193,706	Mar. 12, 1940	Atwood, J. G.
2,197,865	Apr. 23, 1940	Johnson, H. B.
2,198,972	Apr. 30, 1940	Peddrick, C. H., Jr., *et al.*
2,236,548	Apr. 1, 1941	Prouty, W. B.
2,381,514	Aug. 7, 1945	Phelps, D. S.

TABLE 12. U. S. PATENTS ON FLOTATION OF PHOSPHATE ROCK

Patent No.	Date	Patentee
1,467,354	Sept. 11, 1923	Christensen, N. C.
1,492,904	May 6, 1924	Sulman, H. L., *et al.*
1,547,732	July 28, 1925	Broadbridge, W., *et al.*
1,689,693	Oct. 30, 1928	Shapley, C.
1,761,546	June 3, 1930	Trotter, W., *et al.*
1,780,022	Oct. 28, 1930	Littleford, J. W.
1,795,100	Mar. 3, 1931	Trotter, W., *et al.*
1,797,356	Mar. 24, 1931	Martin, R. B.
1,838,422	Dec. 29, 1931	Littleford, J. W., *et al.*
1,912,433	June 6, 1933	Crago, A., *et al.*
1,912,434	do	do
1,914,694	June 20, 1933	Lange, L. H.
1,914,695	do	do
1,927,939	Sept. 26, 1933	Johnston, F. F.
1,958,320	May 8, 1934	Singleton, J. T.
1,968,008	July 24, 1934	Chapman, G. A., *et al.*
1,968,876	Aug. 7, 1934	Crago, A., *et al.*
1,969,269	do	Keller, C. H.

TABLE 12—*Continued*

Patent No.	Date	Patentee
1,970,508	Aug. 14, 1934	Christmann, L. J., *et al.*
1,973,439	Sept. 11, 1934	Mason, A. J.
1,996,021	March 26, 1935	Klosky, S.
1,996,035	do	Singleton, J. T.
2,017,468	Oct. 15, 1935	McCoy, G. H., *et al.*
2,047,773	July 14, 1936	Greene, E. W.
2,069,182	Jan. 26, 1937	Hagood, J.
2,084,413	June 22, 1937	Siems, H. B.
2,113,727	Apr. 12, 1938	Hall, J. P.
2,125,631	Aug. 2, 1938	Gutzeit, G.
2,125,852	do	Ralston, A. W., *et al.*
2,126,292	Aug. 9, 1938	Tartaron, F. X.
2,132,902	Oct. 11, 1938	Lenher, S.
2,134,410	Oct. 25, 1938	Kraus, M.
2,141,862	Dec. 6, 1938	Hall, R. G.
2,142,206	Jan. 3, 1939	Patck, J. M.
2,142,207	do	Price, J. D.
2,148,446	Feb. 28, 1939	Drake, L. D.
2,149,546	Mar. 7, 1939	Ralston, A. W., *et al.*
2,154,092	Apr. 11, 1939	Huns, J. E.
2,162,494	June 13, 1939	Trotter, W., *et al.*
2,162,495	do	do
2,162,525	do	Breerwood, C. H.
2,163,701	June 27, 1939	Reid, R. C.
2,163,702	do	do
2,164,063	do	Handy, R. S.
2,165,268	July 11, 1939	Yogel-Jorgensen, M.
2,166,093	July 11, 1939	Harwood, J., *et al.*
2,168,942	Aug. 8, 1939	McClave, J. M.
2,167,788	Aug. 1, 1939	Weinig, A. J.
2,175,093	Oct. 3, 1939	Ralston, A. W., *et al.*
2,178,239	Oct. 31, 1939	McKenna, W. J.
2,179,622	Nov. 14, 1939	Garrett, A. H.
2,180,278	do	Ellis, R. S.
2,184,115	Dec. 19, 1939	Coke, H. W.
2,185,224	Jan. 2, 1940	Ralston, O. C.
2,185,968	do	Ralston, A. W., *et al.*
2,190,852	Feb. 20, 1940	Tucker, S.
2,194,522	Mar. 26, 1940	Harris, B. R.
2,198,296	Apr. 23, 1940	Thoreau, J. W.
2,198,915	Apr. 30, 1940	MacAfee, M. W.
2,202,484	May 21, 1940	Emery, A. B.
2,202,601	May 28, 1940	Ried, R. C.
2,203,739	June 11, 1940	Ott, E.
2,205,194	June 18, 1940	Green, W. D.
2,205,923	June 25, 1940	Doerner, H. A., *et al.*
2,206,574	July 2, 1940	Pearson, A.
2,216,040	Sept. 24, 1940	Mead, H. L., & Maust, E. J.
2,216,992	Oct. 8, 1940	Vogel-Jorgensen, M.

TABLE 12—*Continued*

Patent No.	Date	Patentee
2,217,684	Oct. 15, 1940	Kirby, J. E., *et al.*
2,217,685	do	do
2,221,088	Nov. 12, 1940	Traylor, J. A.
2,221,485	do	Kirby, J. E., *et al.*
2,222,728	Nov. 26, 1940	Tartaron, F. X.
2,223,679	Dec. 3, 1940	Ellis, R. S.
2,226,170	Dec. 24, 1940	Lasseter, F. P.
2,229,272	Jan. 21, 1941	Booth, R. B.
2,231,066	Feb. 11, 1941	Greene, E. W., *et al.*
2,231,265	do	Gaudin, A. M.
2,238,439	Apr. 15, 1941	Bishop, W. T.
2,246,260	June 24, 1941	Weinig, A. J.
2,251,217	July 29, 1941	Woodhouse, J. C.
2,252,576	Aug. 12, 1941	MacIntosh, J. C.
2,255,139	Sept. 9, 1941	Vogel-Jorgensen, M.
2,258,507	Oct. 7, 1941	Hoag, E. H.
2,259,243	Oct. 14, 1941	Daman, A. C.
2,259,744	Oct. 21, 1941	Fortune, R.
2,267,307	Dec. 23, 1941	Ralston, A. W., *et al.*
2,278,060	Mar. 31, 1942	Christmann, L. J., *et al.*
2,278,107	do	Jayne, D. W., Jr., *et al.*
2,288,237	June 30, 1942	Greene, E. W.
2,289,741	July 14, 1942	Tartaron, F. X.
2,291,031	July 28, 1942	Farenwald, A. W.
2,291,095	do	McLean, L.
2,293,033	Aug. 18, 1942	Mead, H. L., *et al.*
2,293,469	do	Maust, E. J., *et al.*
2,239,470	do	Mead, H. L., *et al.*
2,293,640	do	Crago, A.
2,294,323	Aug. 25, 1942	Wigton, P. I.
2,295,495	Sept. 8, 1942	Erickson, S. E.
2,296,368	Sept. 22, 1942	Ralston, A. W.
2,297,689	Oct. 6, 1942	O'Meara, R. G.
2,298,281	Oct. 13, 1942	Corley, H. M., *et al.*
2,303,931	Dec. 1, 1942	Greene, E. W., *et al.*
2,304,270	Dec. 8, 1942	Mead, H. L., *et al.*
2,305,502	Dec. 15, 1942	Tartaron, F. X.
2,307,397	Jan. 5, 1943	Falconer, S. A., *et al.*
2,310,240	Feb. 9, 1943	Keck, W. E.
2,311,527	Feb. 16, 1943	Frantz, P. M., *et al.*
2,312,387	Mar. 2, 1943	Christmann, L. J., *et al.*
2,312,414	do	Jayne, D. W., *et al.*
2,312,466	do	Erickson, S. E., *et al.*
2,313,360	Mar. 9, 1943	Ralston, A. W., *et al.*
2,316,770	Apr. 20, 1943	Daman, A. C., *et al.*
2,321,186	June 8, 1943	Christmann, L. J., *et al.*
2,322,201	June 15, 1943	Jayne, D. W., Jr., *et al.*
2,324,018	July 13, 1943	Petersen, L. S.
2,327,408	Aug. 24, 1943	Ellis, E. J.

TABLE 12—*Concluded*

Patent No.	Date	Patentee
2,330,587	Sept. 28, 1943	Jayne, D. W., Jr.
2,331,722	Oct. 12, 1943	Patck, J. M.
2,336,014	Dec. 7, 1943	Jayne, D. W., Jr., *et al.*
2,336,015	do	do
2,336,437	do	Erickson, S. E.
2,336,868	Dec. 14, 1943	Jayne, D. W., Jr., *et al.*
2,337,118	Dec. 21, 1943	Lontz, J. F.
2,337,806	Dec. 28, 1943	Farenwald, A. W.
2,343,274	Mar. 7, 1944	Bailey, T. S., Jr., *et al.*
2,349,094	May 16, 1944	Heilmann, T.
2,350,943	June 6, 1944	Thompson, J. W., *et al.*
2,356,821	Aug. 29, 1944	Christmann, L. J., *et al.*
2,362,276	Nov. 7, 1944	Jayne, D. W., Jr., *et al.*
2,362,432	do	Cahn, F. J.
2,364,272	Dec. 5, 1944	Christmann, L. J., *et al.*
2,365,084	Dec. 12, 1944	Jayne, D. W., Jr., *et al.*
2,368,968	Feb. 6, 1945	Christmann, L. J.
2,369,311	Feb. 13, 1945	Mead, H. L., *et al.*
2,369,401	do	Morash, N.
2,370,058	Feb. 20, 1945	Maguire, M. J.
2,373,688	Apr. 17, 1945	Keck, W. E.
2,377,129	May 29, 1945	Christmann, L. J., *et al.*
2,380,698	July 31, 1945	Jayne, D. W., Jr., *et al.*
2,382,178	Aug. 14, 1945	Schilling, K. F., *et al.*
2,383,659	Aug. 28, 1945	Clemmer, J. B., *et al.*
2,384,825	Sept. 18, 1945	Ellis, E. J.
2,389,763	Nov. 27, 1945	Cahn, F. J.
2,400,213	May 14, 1946	Schilling, K. F.
2,401,745	June 11, 1946	Brown, J. B.
2,406,423	Aug. 27, 1946	Farenwald, A. W.
2,406,532	do	do
2,411,288	Nov. 19, 1946	Morse, A. R.
2,414,199	Jan. 14, 1947	Gutzeit, G.
2,416,909	Mar. 4, 1947	Crawford, B. D., *et al.*
2,419,497	Apr. 22, 1947	Meyer, S. E.
2,424,402	July 22, 1947	Loane, C. M., *et al.*
2,424,552	July 29, 1947	Clemmer, J. B., *et al.*
2,433,258	Dec. 23, 1947	Booth, R. B., *et al.*
2,459,219	Jan. 18, 1948	Duke, J. B.
2,459,966	Jan. 25, 1948	Schilling, K. F.
2,459,967	do	do
2,461,813	Feb. 15, 1948	Duke, J. B.
2,461,817	do	Greene, E. W. and Duke, J. B.
2,466,671	Apr. 12, 1949	Gieseke, E. W.
2,466,995	do	McMurray, L. L.
2,494,132	Jan. 10, 1950	Jayne, D. W., *et al.*
2,496,050	Jan. 31, 1950	Herkenhoff, E. C.
2,502,497	Apr. 4, 1950	Wigton, P. L.
2,525,146	Oct. 3, 1950	McMurray, L. L., *et al.*

TABLE 13. U. S. PATENTS ON THE MANUFACTURE OF PHOSPHORUS AND
PHOSPHORIC ACID BY THE VOLATILIZATION PROCESS

Patent No.	Date	Patentee
171,813	Jan. 4, 1876	Hunter, A. G.
239,394	Mar. 29, 1881	Maxim, H. F.
393,428	Nov. 27, 1888	Giles, W. B., *et al.*
417,943	Dec. 24, 1889	Readman, J. B.
452,821	May 26, 1891	Wing, H. H.
455,376	July 7, 1891	do
540,124	May 28, 1895	VanRuymbeke, J.
588,267	Aug. 17, 1897	De Chalmot, G.
602,747	Apr. 19, 1898	Harding, C. K.
669,271	Mar. 5, 1901	VanDenberg, F. P.
689,286	Dec. 17, 1901	DeChalmot, G.
733,017	July 7, 1903	Duncan, R. K.
733,316	do	do
751,753	Feb. 9, 1904	Powten, N. B.
789,438	May 9, 1905	Machalske, F. J.
789,439	do	do
789,440	do	do
859,086	July 2, 1907	Landis, G. C.
862,092	July 30, 1907	Morehead, J. T.
862,093	do	do
902,157	Oct. 27, 1908	Maywald, F. J.
939,078	Nov. 2, 1909	Peacock, S.
984,769	Feb. 21, 1911	Levi, G.
988,137	Mar. 28, 1911	Peacock, S.
995,897	June 20, 1911	do
997,086	July 4, 1911	do
1,000,290	Aug. 8, 1911	do
1,000,311	do	Washburn, F. S.
1,015,707	Jan. 23, 1912	Peacock, S.
1,018,186	Feb. 20, 1912	Haff, M. M.
1,047,864	Dec. 17, 1912	Washburn, F. S.
1,076,497	Oct. 21, 1913	Haff, M. M.
1,076,499	do	Haff, M. M. *et al.*
1,084,856	Jan. 20, 1914	Haff, M. M.
1,100,639	June 16, 1914	Washburn, F. S.
1,103,910	July 14, 1914	Willson, T. L., *et al.*
1,112,211	Sept. 29, 1914	Hechenbleikner, I.
1,129,504	Feb. 23, 1915	Peacock, S.
1,129,514	do	do
1,129,722	do	do
1,142,371	June 8, 1915	Schmitz, F. C.
1,142,397	do	Burroughs, J. W.
1,149,233	Aug. 10, 1915	Washburn, F. S.
1,167,755	Jan. 11, 1916	Heckenbleikner, I.
1,168,495	Jan. 18, 1916	Gray, J. J., Jr.
1,172,420	Feb. 22, 1916	Bassett, H. P.
1,173,960	Feb. 29, 1916	Hechenbleikner, I.
1,202,837	Oct. 31, 1916	do

TABLE 13—*Continued*

Patent No.	Date	Patentee
1,217,306	Feb. 27, 1917	Hechenbleikner, L.
1,220,416	Mar. 27, 1917	Gray, J. J.
1,241,791	Oct. 20, 1917	Waggaman, W. H., *et al.*
1,242,987	Oct. 16, 1917	Schmitz, F. C.
1,274,479	Aug. 6, 1918	Wenman, H. O. H.
1,281,363	Oct. 15, 1918	Haslup, E. W.
1,282,994	Oct. 29, 1918	Waggaman, W. H., *et al.*
1,285,575	Nov. 26, 1918	Allen, W. H.
1,299,336	Apr. 1, 1919	Hechenbleikner, I.
1,299,337	do	do
1,314,229	Aug. 26, 1919	Washburn, F. S.
1,334,474	Mar. 23, 1920	Waggaman, W. H.
1,359,211	Nov. 16, 1920	Washburn, F. S.
1,360,248	Nov. 23, 1920	Brobst, G. R.
1,368,379	Feb. 15, 1921	Allen, W. H.
1,373,471	Apr. 5, 1921	Washburn, F. S.
1,387,817	Aug. 16, 1921	Waggaman, W. H., *et al.*
1,409,295	May 14, 1922	Hechenbleikner, I.
1,410,550	May 28, 1922	Carothers, J. N.
1,422,699	July 11, 1922	Guernsey, E. W., *et al.*
1,441,573	Jan. 9, 1923	Franchot, R., *et al.*
1,457,810	June 5, 1923	Alwart, P. J.
1,463,959	Aug. 7, 1923	Klugh, B. G.
1,468,741	Sept. 5, 1923	Peacock, S.
1,492,712	May 6, 1924	Klugh, B. G.
1,492,713	do	do
1,496,230	June 3, 1924	do
1,497,173	June 10, 1924	Hechenbleikner, I.
1,497,727	June 17, 1924	Klugh, B. G.
1,513,088	Oct. 28, 1924	Charlton, H. W.
1,518,019	Dec. 2, 1924	Tolman, R. D.
1,586,115	May 25, 1926	Pistor, G., *et al.*
1,606,319	Nov. 9, 1926	Parsons, C. E., *et al.*
1,622,082	Mar. 22, 1927	Brassert, H. A., *et al.*
1,622,206	do	Pistor, G.
1,630,283	May 31, 1927	Waggaman, W. H., *et al.*
1,659,146	Feb. 14, 1928	Klugh, B. G.
1,673,691	June 12, 1928	Liljenroth, F. G.
1,680,625	Aug. 14, 1928	Lang, H.
1,692,787	Nov. 20, 1928	Pistor, G., *et al.*
1,695,558	Dec. 18, 1928	Noble, A.
1,700,708	Jan. 29, 1929	Pistor, G., *et al.*
1,701,286	Feb. 5, 1929	Waggaman, W. H.
1,714,685	May 28, 1929	Mathey, E. DuB., *et al.*
1,721,868	July 23, 1929	Mayer, M.
1,723,791	Aug. 6, 1929	Kyber, W.
1,728,948	Sept. 24, 1929	Waggaman, W. H., *et al.*
1,758,241	May 13, 1930	Such, R.
1,766,785	June 24, 1930	Griessback, R.

<div align="center">Table 13—Concluded</div>

Patent No.	Date	Patentee
1,772,849	Aug. 12, 1930	Walton, J. W.
1,775,802	Sept. 16, 1930	Baily, T. F.
1,777,582	Oct. 7, 1930	Seyfried, W. R.
1,795,173	Mar. 3, 1931	Lehrecke, H.
1,797,726	Mar. 24, 1931	Larsson, M.
1,807,790	June 2, 1931	Liljenroth, F. G.
1,814,568	July 14, 1931	Pike, R. D., *et al.*
1,815,379	July 21, 1931	Pike, R. D.
1,818,644	Aug. 11, 1931	Noyes, H. F., *et al.*
1,818,662	do	Weigel, R., *et al.*
1,820,606	Aug. 25, 1931	Easterwood, H. W.
1,836,618	Dec. 15, 1931	Pokorny, E.
1,849,124	Mar. 15, 1932	Urbain, E.
1,900,287	Mar. 17, 1933	Johnson, E.
1,938,551	Dec. 5, 1933	Gooch, S. D., *et al.*
1,951,984	Mar. 20, 1934	Kerschbaum, F. P., *et al.*
1,952,004	do	Weigel, R.
1,959,086	May 15, 1934	Skinner, L. B.
1,961,691	June 5, 1934	Ipater, V. N., *et al.*
1,984,674	Dec. 18, 1934	Fiske, A. H., *et al.*
1,988,387	Jan. 15, 1935	Mason, A. J.
1,990,233	Feb. 5, 1935	Heckenbleikner, I.
2,000,627	May 7, 1935	Udy, M. J.
2,020,976	Nov. 12, 1935	do
2,029,633	Feb. 4, 1936	Kerschbaum, F. P., *et al.*
2,039,297	May 5, 1936	Curtis, H. A.
2,059,796	Aug. 11, 1936	Kerschbaum, F. P., *et al.*
2,059,797	do	do
2,069,225	Feb. 2, 1937	Curtis, H. A.
2,072,981	Mar. 9, 1937	do
2,075,212	Mar. 30, 1937	Levermore, C. L., *et al.*
2,100,843	Nov. 30, 1937	Fischer, S.
2,117,301	May 17, 1938	Curtis, H. A.
2,135,486	Nov. 8, 1938	Almond, L. H.
2,143,001	Jan. 10, 1939	Curtis, H. A., *et al.*
2,150,261	Mar. 14, 1939	Blackwell, H. P., *et al.*
2,153,953	Apr. 11, 1939	Burke, G. W.
2,397,951	Apr. 9, 1946	DeWitte, T. W.
2,399,120	Apr. 23, 1946	Hurd, L. C.
2,488,078	Nov. 15, 1949	Conradi, L. A., *et al.*
2,488,604	Nov. 22, 1949	Pike, R. D.

<div align="center">Table 14. U. S. Patents on Processes and Apparatus Related to the Recovery of Volatilized Phosphorus and Phosphoric Acid</div>

Patent No.	Date	Patentee
171,813	Jan. 4, 1876	Hunter, A. G.
282,118	July 31, 1883	Reese, Jacob
588,267	Aug. 17, 1897	De Chalmot, G.

TABLE 14—*Continued*

Patent No.	Date	Patentee
638,548	Dec. 5, 1899	Billiaudot, L. L.
724,142	Mar. 31, 1903	Stevenson, J., Jr.
1,044,957	Nov. 19, 1912	Washburn, F. S.
1,089,784	Mar. 10, 1914	Peacock, S.
1,115,471	Oct. 27, 1914	Miller, D. I.
1,129,513	Feb. 23, 1915	Peacock, S.
1,142,371	June 8, 1915	Schmitz, F. C.
1,142,397	do	Burroughs, J. W.
1,149,233	Aug. 10, 1915	Washburn, F. S.
1,168,495	Jan. 18, 1916	Gray, J. J., Jr.
1,173,960	Feb. 29, 1916	Hechenbleikner, I.
1,194,077	Aug. 8, 1916	Ross, W. H., *et al.*
1,202,837	Oct. 31, 1916	Hechenbleikner, I.
1,216,306	Feb. 20, 1917	Gray, J. J., Jr.
1,217,306	Feb. 27, 1917	Hechenbleikner, I.
1,226,264	May 15, 1917	Schmitz, F. C.
1,241,791	Oct. 2, 1917	Waggaman, W. H., *et al.*
1,242,987	Oct. 16, 1917	Schmitz, F. C.
1,249,392	Dec. 11, 1917	Hechenbleikner, I.
1,264,236	Apr. 30, 1918	Webster, H. A.
1,264,237	do	do
1,264,510	do	Hechenbleikner, I.
1,264,511	do	do,
1,265,149	May 7, 1918	Webster, H. A.
1,268,849	June 11, 1918	Jeffs, L. A.
1,282,994	Oct. 29, 1918	Waggaman, W. H., *et al.*
1,283,398	do	Carothers, J. N., *et al.*
1,284,200	Nov. 5, 1918	Merz, A. R., *et al.*
1,299,336	Apr. 1, 1919	Hechenbleikner, I.
1,314,229	Aug. 26, 1919	do
1,325,145	Dec. 16, 1919	Davis, J. D.
1,329,273	Jan. 27, 1920	Ross, W. H.
1,373,471	Apr. 5, 1921	Washburn, F. S.
1,381,783	June 14, 1921	Bartleson, T. L.
1,387,817	Aug. 16, 1921	Waggaman, W. H., *et al.*
1,427,436	Aug. 29, 1922	Bradley, E. F.
1,430,619	Oct. 3, 1922	Bradley, L.
1,430,971	do	Fornander, E.
1,440,886	Jan. 2, 1923	Nesbit, A. F.
1,440,887	do	do
1,441,573	Jan. 9, 1923	Franchot, R., *et al.*
1,442,033	do	Sem, M. O., *et al.*
1,442,052	Jan. 16, 1923	Dane, L.
1,443,439	Jan. 30, 1923	Southgate, G. T.
1,445,662	Feb. 20, 1923	Bradley, L.
1,451,418	Apr. 10, 1923	Dillon, E. P., *et al.*
1,462,732	July 24, 1923	Andreau, R. L.
1,469,275	Oct. 2, 1923	Moller, E., *et al.*

TABLE 14—*Continued*

Patent No.	Date	Patentee
1,470,968	Oct. 16, 1923	Gooch, S. D.
1,472,231	Oct. 30, 1923	Schmidt, W. A.
1,477,454	Dec. 11, 1923	Seibert, H.
1,496,230	June 3, 1924	Klugh, B. G.
1,496,231	do	do
1,496,232	do	do
1,496,674	do	Helfenstein, A.
1,497,727	June 17, 1924	Klugh, B. G.
1,513,890	Nov. 4, 1924	Bryan, H., *et al.*
1,514,912	Nov. 11, 1924	Klugh, B. G.
1,534,828	Apr. 21, 1925	Barr, J. A.
1,538,089	May 19, 1925	Carothers, J. N.
1,545,975	July 14, 1925	Rathbun, R. B.
1,583,054	May 4, 1926	Klugh, B. G.
1,584,055	May 11, 1926	Weiskopf, C. H.
1,592,616	July 13, 1926	Noyes, H. F.
1,593,514	July 20, 1926	Suchy, R.
1,598,259	Aug. 31, 1926	Ross, W. H., *et al.*
1,605,548	Nov. 2, 1926	Cooke, M. W.
1,613,125	Jan. 4, 1927	Rawn, E. V.
1,622,206	Mar. 22, 1927	Pistor, J. G.
1,634,570	July 5, 1927	Boynton, A. J.
1,634,796	do	Miner, C. G.
1,646,268	Oct. 18, 1927	Warner, J.
1,650,097	Nov. 22, 1927	Schmidt, W. A.
1,655,981	Jan. 10, 1928	Barr, J. A.
1,659,146	Feb. 14, 1928	Perere, E. F.
1,659,198	do	Griessback, R.
1,686,873	Oct. 9, 1928	Miner, C. G.
1,688,503	Oct. 23, 1928	do
1,688,822	do	Maxwell, J., *et al.*
1,698,484	Jan. 8, 1929	Urbain, E.
1,721,868	July 23, 1929	Mayer, M.
1,730,521	Oct. 8, 1929	Miner, C. G.
1,732,373	Oct. 22, 1929	Mittasch, A.
1,756,429	Apr. 29, 1930	Larsson, M.
1,758,404	May 13, 1930	Labbe, A. L.
1,766,421	June 24, 1930	Wintermute, H. A., *et al.*
1,773,835	Aug. 26, 1930	do
1,773,840	do	Nattcher, A., *et al.*
1,773,876	do	Seipp, F.
1,777,548	Oct. 7, 1930	Booth, C. F.
1,788,838	Jan. 13, 1931	Lang, H.
1,791,338	Feb. 3, 1931	Wintermute, H. A.
1,794,074	Feb. 24, 1931	Hedberg, C. W. J., *et al.*
1,794,615	Mar. 3, 1931	Hoss, W.
1,794,616	do	do
1,798,511	Mar. 31, 1931	Wintermute, H. A., *et al.*

TABLE 14—*Concluded*

Patent No.	Date	Patentee
1,800,529	Apr. 14, 1931	Horne, G. H.
1,807,767	June 2, 1931	Conway, B. V. G., *et al.*
1,810,614	June 16, 1931	Knight, A. P.
1,811,602	June 23, 1931	Woodstock, W. H., *et al.*
1,813,306	July 7, 1931	Marshall, K. I.
1,815,581	July 21, 1931	Paukner, G., *et al.*
1,820,726	Aug. 25, 1931	Bayha, H., *et al.*
1,848,579	Mar. 8, 1932	Seipp, F.
1,848,813	do	Woodstock, W. H., *et al.*
1,852,959	Apr. 5, 1932	Dutoit, P.
1,860,818	May 31, 1932	Rohre, K., *et al.*
1,863,507	June 14, 1932	Southgate, G. T.
1,875,755	Sept. 6, 1932	Noyes, H. F.
1,880,538	Oct. 4, 1932	Waggaman, W. H., *et al.*
1,882,517	Oct. 11, 1932	Neumark, M., *et al.*
1,903,640	Apr. 11, 1933	Wintermute, H. A.
1,903,644	do	Meston, A. F.
1,940,758	Dec. 26, 1933	Lehrecke, H.
2,003,725	June 4, 1935	Skinner, L. B.
2,029,309	Feb. 4, 1936	Curtis, H. A., *et al.*
2,040,081	May 12, 1936	Curtis, H. A.
2,069,692	Feb. 2, 1937	Wintermute, H. A.
2,100,155	Nov. 23, 1937	Beran, V.
2,101,168	Dec. 7, 1937	Deutsch, W.
2,110,631	Mar. 1, 1938	Meston, A. F.
2,157,017	May 2, 1939	Rue, O. P.
2,199,390	May 7, 1940	Anderson, E.
2,245,576	June 3, 1941	Wintermute, H. A.
2,251,451	Aug. 5, 1941	Heinrich, R.
2,289,538	July 7, 1942	Buford, E. H.
2,359,243	Sept. 26, 1944	Pernert, J. C.
2,397,951	Apr. 9, 1946	DeWitte, T. W.
2,399,120	Apr. 23, 1946	Hurd, L. C.
2,467,039	Apr. 12, 1949	Kerschbaum, F. P., *et al.*
2,476,418	July 19, 1949	Klugh, B. G.
2,488,078	Nov. 15, 1949	Conradi, L. A., *et al.*
2,488,604	Nov. 22, 1949	Pike, R. D.

TABLE 15. U. S. PATENTS ON THE OXIDATION OF PHOSPHORUS

Patent No.	Date	Patentee
1,242,987	Oct. 16, 1917	Schmitz, F. C.
1,249,392	Dec. 11, 1917	Hechenbleikner, I.
1,325,145	Dec. 16, 1919	Davis, J. D.
1,463,959	Aug. 11, 1923	Klugh, B. G.
1,497,173	June 10, 1924	Hechenbleikner, I.
1,594,372	Aug. 3, 1926	Liljenroth, F. G.
1,605,960	Nov. 9, 1926	do
1,634,570	July 5, 1927	Boynton, A. J.

TABLE 15—*Concluded*

Patent No.	Date	Patentee
1,668,539	May 1, 1928	Larsson, M.
1,673,691	June 12, 1928	Liljenroth, F. G.
1,698,484	Jan. 8, 1929	Urbain, E.
1,700,708	Jan. 29, 1929	Pistor, G., *et al.*
1,732,373	Oct. 22, 1929	Mittasch, A., *et al.*
1,756,429	Apr. 29, 1930	Larsson, M.
1,797,726	Mar. 24, 1931	do
1,815,581	July 21, 1931	Panckner, G., *et al.*
1,818,644	Aug. 11, 1931	Noyes, H. F., *et al.*
1,823,923	Sept. 22, 1931	Wild, W., *et al.*
1,848,295	Mar. 8, 1932	Ipatieff, W. N.
1,856,144	May 3, 1932	Wietzel, G., *et al.*
1,879,189	Sept. 27, 1932	Gooch, S. D., *et al.*
1,895,329	Jan. 24, 1933	Ipatieff, W., *et al.*
1,916,594	July 4, 1933	Weitzel, G., *et al.*
1,991,916	Feb. 19, 1935	Zinn, Robt. E.
2,107,857	Feb. 8, 1938	Emmett, P. H.
2,110,870	Mar. 15, 1938	Curtis, H. A.
2,113,574	Apr. 12, 1938	do
2,125,297	Aug. 2, 1938	Junkins, J. N.
2,132,360	Oct. 4, 1938	Merchant, M. H.
2,132,592	Oct. 11, 1938	Wells, J. E., *et al.*
2,221,770	Nov. 19, 1940	Almond, L. H.
2,247,373	July 1, 1941	Hartford, C. E., *et al.*
2,272,402	Feb. 10, 1942	DuBois, G.
2,272,414	do	McCullough, C. R.
2,374,188	Apr. 24, 1945	Frear, G. L.
2,499,374	Mar. 7, 1950	Elmore, K. L.
2,499,424	do	Shultz, J. F.

TABLE 16. U. S. PATENTS ON THE MANUFACTURE OF PHOSPHORIC ACID BY THE SULFURIC ACID OR "WET PROCESS"

Patent No.	Date	Patentee
137,635	Apr. 8, 1873	Storck, H., *et al.*
276,143	Apr. 17, 1883	Knight, J. J.
459,575	Sept. 15, 1891	Glaser, C.
629,996	Aug. 1, 1899	Holtmann, J.
917,502	Apr. 6, 1909	Strickle
1,018,746	Feb. 27, 1912	Dittmar, M.
1,083,429	Jan. 6, 1914	Brunschwig, F.
1,499,611	July 1, 1924	Gravell, J. H.
1,590,655	June 29, 1926	Spicer, H. N.
1,648,137	Nov. 8, 1927	Larison, E. L.
1,655,019	Jan. 3, 1928	Mantius, O.
1,663,734	Mar. 27, 1928	Stroder, E.
1,667,549	Apr. 24, 1928	Hechenbleikner, I.
1,688,679	Oct. 23, 1928	Baum, G.
1,690,363	Nov. 6, 1928	Egleson, J. E.
1,695,619	Dec. 18, 1928	Trautman, O. C.

TABLE 16—*Concluded*

Patent No.	Date	Patentee
1,702,192	Feb. 12, 1929	Bloomfield, A. L., *et al.*
1,702,193	do	do
1,718,871	June 25, 1929	Nordell, C. H.
1,756,637	Apr. 29, 1930	Edwards, R. S.
1,765,252	June 17, 1939	Vernay, J. B.
1,770,367	July 8, 1930	Edwards, R. S.
1,776,595	Sept. 23, 1930	Nordengren, S. G.
1,787,101	Dec. 30, 1930	Branwell, F. H.
1,790,220	Jan. 27, 1931	Balz, O., *et al.*
1,836,694	Dec. 15, 1931	Wadsted, B.
1,838,431	Dec. 29, 1931	Milligan, C. H.
1,850,017	Mar. 15, 1932	Lehrecke, H.
1,851,179	Mar. 29, 1932	Hechenbleikner, I.
1,857,470	Mar. 10, 1932	Milligan, C. H., *et al.*
1,860,527	May 31, 1932	Bryan, C. S.
1,889,949	Dec. 6, 1932	Clark, C. B.
1,894,514	Jan. 17, 1933	Hechenbleikner, I.
1,902,648	Mar. 21, 1933	Larsson, M.
1,916,431	July 4, 1933	Larsson, M.
1,929,441	Oct. 10, 1933	Milligan, C. H.
1,929,442	do	do
1,929,443	do	do
1,940,689	Dec. 26, 1933	Moore, G. F.
1,944,048	Jan. 16, 1934	Walker, G. E., *et al.*
1,969,449	Aug. 7, 1934	Bryan, C. S.
1,981,145	Nov. 20, 1934	Keller, C. H.
2,013,970	Sept. 10, 1935	Moore, G. F.
2,049,032	July 28, 1936	Weber, W. C., *et al.*
2,064,833	Dec. 22, 1936	Howard, H.
2,169,588	Aug. 15, 1939	Malawan, J. E.
2,169,589	do	do
2,384,773	Sept. 11, 1945	Shoeld, M.
2,384,813	Sept. 18, 1945	Coleman, J. H.
2,384,814	do	do
2,504,544	Apr. 18, 1950	Legal, C. C., Jr., *et al.*
2,531,977	Nov. 28, 1950	Hammaran, B. W., *et al.*

TABLE 17. U. S. PATENTS ON THE PURIFICATION OF PHOSPHORIC ACID FOR FOOD AND CHEMICAL PURPOSES

Patent No.	Date	Patentee
14,722	Apr. 22, 1856	Horsford, E. N.
75,271	Mar. 10, 1868	Horsford, E. N., *et al.*
75,272	do	do
75,332	do	Wilson, G. F.
75,338	do	do
75,339	do	do
76,763	Apr. 14, 1868	Horsford, E. N.
130,298	Aug. 6, 1872	do
132,298	Oct. 15, 1872	Lesner, A. C.

TABLE 17—*Continued*

Patent No.	Date	Patentee
137,635	July 1, 1873	Storck, H., *et al.*
164,457	June 15, 1875	Jas, A.
418,259	Dec. 31, 1889	Winssinger, C. E. D.
446,815	Feb. 17, 1891	Glaser, C.
598,182	Feb. 1, 1898	Poole, H.
1,018,746	Feb. 27, 1912	Dittmar, M.
1,083,429	Jan. 6, 1914	Brunschwig, F.
1,149,233	Aug. 10, 1915	Washburn, F. S.
1,283,398	Oct. 29, 1918	Carothers, J. N., *et al.*
1,329,273	Jan. 27, 1920	Ross, W. H.
1,383,990	July 5, 1921	Kelly, A.
1,451,786	Apr. 17, 1923	Ross, W. H., *et al.*
1,487,205	Mar. 18, 1924	Carothers, J. N., *et al.*
1,493,099	May 6, 1924	Bramson, C.
1,493,100	do	do
1,499,611	July 1, 1924	Gravell, J. H.
1,511,929	Oct. 14, 1924	Alcock, H. E.
1,538,089	May 19, 1925	Carothers, J. N., *et al.*
1,538,910	May 26, 1925	Stokes, W. E.
1,544,911	July 7, 1925	Laist, F.
1,562,818	Nov. 24, 1925	Wolfes, O.
1,597,984	Aug. 31, 1926	La Bour, H. E.
1,601,208	Sept. 28, 1926	Gerber, A. B.
1,648,137	Nov. 8, 1927	Larison, E. L.
1,648,146	do	Pevere, E. F., *et al.*
1,688,822	Oct. 23, 1928	Hoffman, P. C., *et al.*
1,692,787	Nov. 20, 1928	Pistor, G., *et al.*
1,744,371	Jan. 21, 1930	Draisbach, F.
1,746,905	Feb. 11, 1930	Pike, R. D., *et al.*
1,777,548	Oct. 7, 1930	Booth, C. F.
1,785,473	Dec. 16, 1930	Adler, H., *et al.*
1,787,192	Dec. 30, 1930	Fiske, A. H.
1,788,952	Jan. 13, 1931	Holz, A.
1,818,114	Aug. 11, 1931	Carothers, J. N., *et al.*
1,856,144	May 3, 1932	Weitzel, G., *et al.*
1,858,293	May 10, 1932	Fiske, A. H., *et al.*
1,873,457	Aug. 23, 1932	Muller, W., *et al.*
1,889,929	Dec. 6, 1932	Moore, G. F.
1,894,289	Jan. 17, 1933	Wood, B. F.
1,901,020	Mar. 14, 1933	Booth, C. F.
1,929,476	Oct. 10, 1933	do
1,951,077	Mar. 13, 1934	Woodstock, W. H.
1,968,544	July 31, 1934	Vana, C. A.
1,972,196	Sept. 4, 1934	Larison, E. L.
2,003,051	May 28, 1935	Knox, W. H., Jr.
2,028,632	June 21, 1936	Taylor, G. E.
2,035,850	Mar. 31, 1936	Vivian, R. E.
2,057,956	Oct. 20, 1936	Kaselitz, O.
2,079,847	May 11, 1937	Fiske, A. H.

TABLE 17—*Concluded*

Patent No.	Date	Patentee
2,081,351	May 25, 1937	Booth, C. F.
2,095,994	Oct. 19, 1937	MacIntire, W. H.
2,121,208	June 21, 1938	Milligan, C. H.
2,123,554	July 12, 1938	Klosky, S.
2,123,785	do	Knox, W. H., *et al.*
2,128,182	Aug. 23, 1938	Fiske, A. H.
2,130,579	Sept. 20, 1938	Bowman, F. C.
2,132,349	Oct. 4, 1938	Booth, C. F.
2,160,700	May 30, 1939	Knox, W. H.
2,160,701	do	do
2,165,100	July 4, 1939	Hettrick, A. B.
2,174,158	Sept. 26, 1939	Kepfer, R. J., *et al.*
2,202,526	May 28, 1940	Hixon, A. W., *et al.*
2,220,818	Nov. 5, 1940	Jelen, F. C.
2,271,361	Jan. 27, 1942	Carpenter, F. B., Jr.
2,272,617	Feb. 10, 1942	Cox, E., *et al.*
2,287,264	June 23, 1942	Ogburn, S. C.
2,287,683	do	Hurka, R. J.
2,288,460	do	Kane, J. H., *et al.*
2,288,752	July 7, 1942	Simpson, G. S.
2,302,956	Nov. 24, 1942	Retaillian, E.
2,312,047	Feb. 23, 1943	Ogburn, S. C., Jr.
2,338,407	Jan. 4, 1944	Coleman, J. H., *et al.*
2,338,408	do	do
2,343,456	Mar. 7, 1944	Henniger, A. H.
2,384,813	Sept. 18, 1945	Coleman, J. H.
2,384,814	do ,	do
2,405,884	Aug. 13, 1946	Greger, H. H.
2,415,797	Feb. 11, 1947	Low, F. S.
2,492,714	Dec. 27, 1949	Singer, M. R.
2,493,915	Jan. 10, 1950	Cross, R.
2,514,973	July 11, 1950	Robinson, W. L.

TABLE 18. U. S. PATENTS ON THE MANUFACTURE OF SUPERPHOSPHATE AND ANALOGOUS PRODUCTS

Patent No.	Date	Patentee
16,882	Mar. 24, 1857	Reid, L.
34,825	Apr. 1, 1862	Gallicher, J. M.
38,040	Mar. 31, 1863	Gale, L. D.
41,428	Feb. 2, 1864	Harper, L.
41,663	Feb. 16, 1864	Hayes, A. A.
42,006	Mar. 22, 1864	Liebig, G. A.
46,700	Mar. 7, 1865	Potts, R. B.
59,978	Nov. 27, 1866	Figaniere, A. de
75,325	Mar. 10, 1868	Wilson, G. F.
75,327	do	do
86,289	Jan. 26, 1869	Duvall, A.
90,367	May 25, 1869	Lalor, W.

TABLE 18—*Continued*

Patent No.	Date	Patentee
100,729	Mar. 15, 1870	Commins, J.
105,319	July 12, 1870	Duvall, A.
106,147	Aug. 9, 1870	Frank, E., *et al.*
110,084	Jan. 17, 1870	Spense, P.
113,416	Apr. 4, 1871	Forbes, D., *et al.*
125,613	Apr. 9, 1872	Pratt, N. A.
126,904	May 21, 1872	do
128,752	July 9, 1872	Pratt, N. A., *et al.*
173,621	Feb. 15, 1876	Griffith, A. G.
211,238	Jan. 7, 1879	Jugmanson, J.
246,121	Aug. 23, 1881	Graff, L.
252,029	Jan. 10, 1882	Gibbons, J. F., *et al.*
276,143	Apr. 17, 1883	Knicht, J. J.
278,383	May 29, 1883	Young, J. R.
278,480	do	do
281,635	July 17, 1883	Koefoed, A. H.
301,348	July 1, 1884	Liebig, G., *et al.*
302,266	July 22, 1884	do
305,249	Sept. 16, 1884	Stillman, T. B., *et al.*
317,010	May 5, 1885	Pierce, W. S.
322,698	July 21, 1885	Dibben, F., *et al.*
371,083	Oct. 4, 1887	Lord, V.
374,201	Dec. 6, 1887	Petraeus, C. V.
382,604	May 8, 1888	Goodale, S. L.
395,532	Jan. 1, 1889	Williams, W. J.
407,240	July 16, 1889	Powter, N.
407,241	do	do
445,255	Jan. 27, 1891	Seal, W. B.
445,567	Feb. 3, 1891	Memminger, C. G.
446,998	Feb. 24, 1891	Van Ruymbeke, J.
484,631	Oct. 18, 1892	Dunne, J. J.
494,940	Apr. 4, 1893	Rissmuller, L.
496,687	May 2, 1893	Hoffman, P. C.
515,708	Feb. 27, 1894	Gregory, J.
620,443	Feb. 28, 1899	Goldsmith, W. L.
683,014	Sept. 24, 1901	Augstadt, W. B., *et al.*
690,049	Dec. 31, 1901	Cheeseman, L.
703,295	June 24, 1902	Newport, R. B.
709,185	Sept. 16, 1902	Terne, Bruno
731,461	June 23, 1903	Jarecke, A. K.
736,730	Aug. 18, 1903	Hoyerman, G.
789,647	May 9, 1905	Arens, R.
897,695	Sept. 1, 1908	Young, J. R.
911,283	Sept. 3, 1908	do
995,028	Sept. 30, 1910	Newberry, S. B., *et al.*
997,968	July 18, 1911	Cusatelli, G.
1,003,681	Sept. 19, 1911	Williams, R.
1,014,255	Jan. 9, 1912	Pratt, N. P.

TABLE 18—*Continued*

Patent No.	Date	Patentee
1,020,153	Mar. 12, 1912	Newberry, S. B., *et al.*
1,024,880	Apr. 30, 1912	Coates, L. R.
1,034,090	July 30, 1912	Dunham, H. V.
1,093,141	Apr. 14, 1914	Lynen, G. H.
1,100,638	June 16, 1914	Washburn, F. S.
1,103,115	July 14, 1914	do
1,105,304	July 28, 1914	Reed, E. W.
1,137,531	Apr. 27, 1915	Pratt, G. L.
1,168,255	Jan. 11, 1916	Herzka, E.
1,246,636	Nov. 13, 1917	Meyers, H. H.
1,255,829	Feb. 5, 1918	Blumenberg, H., Jr.
1,375,115	Apr. 19, 1921	Shoeld, M.
1,376,612	May 12, 1921	Forbis, R. E.
1,383,911	July 5, 1921	Doyle, W. T.
1,383,912	do	do
1,385,126	July 19, 1921	Gaston, R. T.
1,398,816	Nov. 29, 1921	Tuttle, A. L.
1,401,527	Dec. 27, 1921	Doyle, W. T.
1,403,820	Jan. 17, 1922	Sturtevant, T. J.
1,413,048	Apr. 18, 1922	Matheson, A.
1,428,920	Sept. 12, 1922	Sturtevant, T. J.
1,428,921	do	do
1,428,922	do	do
1,430,621	Oct. 3, 1922	Bruhn, G. A.
1,439,054	Dec. 19, 1922	Armstrong, E. H.
1,459,124	June 19, 1923	Webster, H. A.
1,461,077	July 10, 1923	do
1,485,406	Mar. 4, 1924	Meyers, H. H.
1,576,022	Mar. 9, 1926	Armstrong, E. H.
1,585,810	May 25, 1926	Williams, F. W. R.
1,604,359	Oct. 26, 1926	Larison, E. L.
1,675,871	July 3, 1928	Wever, F. M.
1,725,694	Aug. 20, 1929	Baker, D. L.
1,761,991	June 3, 1930	Ober, B.
1,761,992	do	do
1,773,287	Aug. 19, 1930	Sturtevant, T. J.
1,782,821	Nov. 25, 1930	Hechenbleikner, I.
1,837,283	Dec. 22, 1931	Ober, B., *et al.*
1,837,284	do	do
1,837,304	do	Wight, E. H.
1,837,305	do	Wight, E. H., *et al.*
1,837,307	do	do
1,837,328	do	Ober, B., *et al.*
1,837,329	do	do
1,837,331	do	do
1,837,332	do	do
1,865,383	June 28, 1932	do
1,867,866	July 19, 1932	do

TABLE 18—*Concluded*

Patent No.	Date	Patentee
1,869,272	July 26, 1932	do
1,869,941	Aug. 2, 1932	do
1,869,952	do	Anderson, D. L.
1,870,278	Aug. 9, 1932	Broadfield, M. D.
1,870,602	do	Case, A. H.
1,871,416	do	Broadfield, M. D.
1,879,435	Sept. 27, 1932	Ober, B., *et al.*
1,880,470	Oct. 4, 1932	do
1,880,544	do	Waggaman, W. H.
1,893,437	Jan. 3, 1933	Ober, B., *et al.*
1,929,710	Oct. 10, 1933	Ober, B., *et al.*
1,959,973	May 22, 1934	Wellish, D.
1,982,479	Nov. 27, 1934	Ober, B., *et al.*
1,982,480	do	Pfaff, G. C.
1,986,293	Jan. 1, 1935	Shoeld, M.
2,010,579	Aug. 6, 1935	Broadfield, M. D.
2,015,384	Sept. 24, 1935	Nordengren, S. G.
2,021,671	Nov. 19, 1935	Skinner, L. B.
2,040,081	May 12, 1936	Curtis, H. A.
2,075,801	Apr. 6, 1937	do
2,100,583	Nov. 30, 1937	Wilson, A.
2,106,223	Jan. 25, 1938	Nordengren, S. G.
2,115,150	Apr. 26, 1938	Seyfried, W. R.
2,136,793	Nov. 15, 1938	Gabeler, W. C., *et al.*
2,148,209	Feb. 21, 1939	Loisean, H., *et al.*
2,213,243	Sept. 3, 1940	Facer, J. L. H.
2,232,145	Feb. 18, 1941	Shoeld, M.
2,233,956	Mar. 4, 1941	Moore, G. F.
2,248,514	July 8, 1941	Shoeld, M.
2,248,515	do	do
2,268,816	Jan. 6, 1942	Gabeler, W. H., *et al.*
2,308,220	Jan. 12, 1943	Waggaman, W. H.
2,384,773	Sept. 11, 1945	Shoeld, M.
2,414,701	Jan. 21, 1947	do
2,416,663	Feb. 25, 1947	Menefee, A. B., *et al.*
2,418,203	Apr. 1, 1947	Stauffer, J., Jr.
2,442,513	June 1, 1948	Sackett, W. J.
2,448,126	Aug. 31, 1948	Shoeld, M.
2,504,546	Apr. 18, 1950	Wight, E. H., *et al.*
2,515,163	July 11, 1950	Mohr, A. C.
2,528,514	Nov. 7, 1950	Harvey, S. A., *et al.*
2,531,798	Nov. 28, 1950	Werner, E. A.

TABLE 18-A. U. S. PATENTS ON CONCENTRATED OR TRIPLE SUPERPHOSPHATE

Patent No.	Date	Patentee
389,566	Sept. 18, 1888	Glaser, W.
417,820	Dec. 24, 1889	do
459,575	Sept. 15, 1891	do

TABLE 18A—*Concluded*

Patent No.	Date	Patentee
631,181	Aug. 15, 1899	Schuler, G.
655,458	Aug. 7, 1900	Saxl, H.
1,078,887	Nov., 1913	Wilson, T. L., *et al.*
1,083,429	Jan. 6, 1914	Brunswig, F.
1,351,672	Aug. 31, 1920	Meigs, C. C.
1,470,968	Oct. 16, 1923	Gooch, S. D.
1,475,959	Dec. 4, 1923	Meyers, H. H.
1,604,359	Oct. 26, 1926	Larison, E. L.
1,668,464	May 1, 1928	Pease, E. L.
1,706,101	Mar. 19, 1929	Blumenberg, A. H.
1,780,620	Nov. 4, 1930	King, W. B.
1,790,502	Jan. 27, 1931	Hechenbleikner, I.
1,823,923	Sept. 22, 1931	Wild, W., *et al.*
1,837,285	Dec. 22, 1931	Ober, B., *et al.*
1,837,330	do	do
1,851,210	Mar. 29, 1932	Palazzo, F. C., *et al.*
1,869,879	Aug. 2, 1932	Balz, O., *et al.*
1,869,952	do	Anderson, D. L.
1,879,435	Sept. 27, 1932	Ober, B., *et al.*
1,880,470	Oct. 4, 1932	do
1,891,007	Dec. 13, 1932	Palazzo, F. C., *et al.*
1,929,452	Oct. 10, 1933	Sebastian, R. L.
2,067,538	Jan. 12, 1937	MacIntire, W. H.
2,070,582	Feb. 16, 1937	Curtis, H. A.
2,072,980	do	do
2,086,565	July 13, 1937	MacIntire, W. H.
2,095,460	Sept. 21, 1937	do
2,093,461	do	do
2,137,674	Nov. 22, 1938	do
2,143,025	Jan. 10, 1939	Newton, R. H.
2,361,444	Oct. 31, 1944	Zbornik, T. W.
2,522,500	Sept. 19, 1950	Bridger, G. L.

TABLE 19. U. S. PATENTS ON AMMONIUM PHOSPHATES AND AMMONIATED SUPERPHOSPHATES

Patent No.	Date	Patentee
39,519	Aug. 11, 1863	Wilson, G. F.
77,840	May 12, 1868	Ramsburgh, J. S.
78,730	June 9, 1868	Fales, L. S.
100,457	Mar. 1, 1870	Shepard, C. U., Jr.
100,729	Mar. 15, 1870	Commins, J.
110,084	Dec. 13, 1870	Spense, Peter
135,995	Feb. 18, 1873	McDougall, John
156,181	Oct. 20, 1874	Siebel, J. E.
206,070	July 16, 1878	Boykin, T. J., *et al.*
450,253	Apr. 14, 1891	Reese, J.
450,255	do	do
709,185	Sept. 16, 1902	Terne, Bruno

TABLE 19—*Continued*

Patent No.	Date	Patentee
897,695	Sept. 1, 1908	Young, J. R.
1,001,350	Aug. 22, 1911	Caro, N., *et al.*
1,036,896	Aug. 27, 1912	Peacock, S.
1,040,081	Oct. 1, 1912	Willson, T. L., *et al.*
1,062,869	May 27, 1913	do
1,100,638	June 16, 1914	Washburn, F. S.
1,103,115	July 14, 1914	do
1,112,183	Sept. 29, 1914	Willson, T. L., *et al.*
1,115,044	Oct. 27, 1914	Washburn, F. S.
1,122,183	Sept. 29, 1914	Willson, T. L., *et al.*
1,127,840	Feb. 9, 1915	do
1,142,068	June 8, 1915	Washburn, F. S.
1,145,107	July 6, 1915	Willson, T. L., *et al.*
1,146,222	July 13, 1915	do
1,151,074	Aug. 24, 1915	Washburn, F. S.
1,151,633	Aug. 31, 1915	do
1,161,473	Nov. 23, 1915	Haff, M. M., *et al.*
1,166,104	Dec. 28, 1915	Willson, T. L., *et al.*
1,167,788	Jan. 11, 1916	Washburn, F. S.
1,194,077	Aug. 8, 1916	Ross, W. H., *et al.*
1,196,910	Sept. 5, 1916	Washburn, F. S.
1,208,877	Dec. 19, 1916	Wollenweber, W.
1,251,742	Jan. 1, 1918	Blumenberg, H., Jr.
1,252,318	do	do
1,258,106	Mar. 5, 1918	Gardiner, R. F.
1,264,513	Apr. 30, 1918	Hechenbleikner, I.
1,264,514	do	do
1,276,870	Aug. 27, 1918	Cameron, F. K.
1,280,650	Oct. 8, 1918	Bosch, C.
1,355,369	Oct. 12, 1920	Washburn, F. S.
1,357,120	Oct. 26, 1920	Sadtler, S. S.
1,367,846	Feb. 8, 1921	Washburn, F. S.
1,369,763	Feb. 22, 1921	Hetherington, H. C., *et al.*
1,417,248	May 23, 1922	Husson, J.
1,418,618	June 6, 1923	Butt, C. A.
1,456,850	May 29, 1924	Hazen, Wm., *et al.*
1,514,912	Nov. 11, 1924	Klugh, B. G.
1,601,233	Sept. 28, 1926	Blumenberg, H., Jr.
1,610,109	Dec. 7, 1926	Peas, E. L., *et al.*
1,628,792	May 17, 1927	Larison, E. L., *et al.*
1,659,198	Feb. 14, 1928	Griessbach, R., *et al.*
1,670,504	May 22, 1928	do
1,716,415	June 11, 1929	Buchanan, G. H.
1,758,448	May 13, 1930	Liljenroth, F. G.
1,761,400	June 3, 1930	do
1,785,375	Dec. 16, 1930	Buchanan, G. H.
1,790,503	Jan. 27, 1931	Hechenbleikner, I.
1,809,473	June 9, 1931	Colbjornsen, B.

TABLE 19—*Concluded*

Patent No.	Date	Patentee
1,822,040	Sept. 8, 1931	Klugh, B. G., *et al.*
1,826,785	Oct. 13, 1931	Holz, August
1,834,418	Dec. 1, 1931	Pevere, E. F.
1,835,441	Dec. 8, 1931	Suchy, R., *et al.*
1,855,856	Apr. 26, 1932	Hansen, C. J.
1,856,187	May 3, 1932	Johnson, E.
1,859,835	May 24, 1932	Mitteau, F.
1,866,564	July 12, 1932	Hanson, C. J.
1,867,866	July 19, 1932	Ober, B., *et al.*
1,869,272	July 26, 1932	do
1,871,195	Aug. 9, 1932	do
1,876,011	Sept. 6, 1932	Larsson, M.
1,876,501	do	Johnson, E.
1,878,997	Sept. 27, 1932	Adelantalo, L.
1,879,204	do	Guillissen, J.
1,880,469	Oct. 4, 1932	Ober, B., *et al.*
1,884,105	Oct. 25, 1932	Moore, H. C.
1,884,751	do	Krase, H. J.
1,907,438	May 9, 1933	Ober, B., *et al.*
1,913,539	June 13, 1933	Friedrich, H.
1,913,791	do	Larsson, M.
1,916,429	July 4, 1933	do
1,945,914	Feb. 6, 1934	Reubke, Emil
1,949,129	Feb. 27, 1934	Oehme, Hermann
1,960,184	May 22, 1934	Sackett, A. J.
1,969,894	Aug. 14, 1934	Liljenroth, F. G.
1,998,631	Apr. 23, 1935	Tramm, H., *et al.*
1,999,026	do	do
2,019,713	Nov. 5, 1935	Lawrence, C. K.
2,022,050	Nov. 26, 1935	Levermore, C. H.
2,037,706	Apr. 21, 1936	Curtis, H. A.
2,040,563	May 12, 1936	Phillips, J. J.
2,051,029	Apr. 18, 1936	Curtis, H. A.
2,053,432	Sept. 8, 1936	Harvey, E. W.
2,353,658	July 18, 1944	Fox, E. J.
2,415,464	Feb. 11, 1947	Crittenden, E. D.
2,504,545	Apr. 18, 1950	Waring, C. E., *et al.*

TABLE 20. U. S. PATENTS ON TREATMENT OF PHOSPHATE ROCK WITH ACIDS OTHER THAN SULFURIC ACID

Patent No.	Date	Patentee
49,831	Sept. 5, 1865	Liebig, G. A.
75,271	Mar. 10, 1868	Horsford, E. N.
75,272	do	do
75,335	do	Wilson, G. F.
75,339	do	do
76,763	Apr. 14, 1868	Horsford, E. N.
140,559	July 1, 1873	Tanner, B.

TABLE 20—*Continued*

Patent No.	Date	Patentee
164,457	June 15, 1875	Jas, A.
196,881	Nov. 6, 1877	Designolle, G. L. G.
279,445	June 12, 1883	Schribler, C.
281,635	July 17, 1883	Koefoed, A. H.
283,427	Aug. 21, 1883	Scribner, E. A.
389,566	Sept. 18, 1888	Glaser, C.
417,820	Dec. 24, 1889	do
504,453	Sept. 5, 1893	Meyer, T.
631,181	Aug. 15, 1899	Schuler, G.
657,717	Sept. 11, 1900	Wharton, J. C.
789,647	May 9, 1905	Arens, R.
852,371	Apr. 30, 1907	Bergman, E.
852,372	do	do
872,757	Dec. 3, 1907	Schlutius, J.
902,425	Oct. 27, 1908	Machalske, F. J.
995,894	June 20, 1911	Palmaer, W.
936,317	Oct. 12, 1909	Halvorsen, B. F.
997,968	July 18, 1911	Cusatelli, G.
1,011,909	Dec. 19, 1911	Bretteville, A.
1,018,746	Feb. 27, 1912	Dittmar, M.
1,020,153	Mar. 12, 1912	Newberry, S. B., *et al.*
1,036,909	Aug. 27, 1912	Saarbach, L.
1,057,876	Apr. 1, 1913	Peacock, S.
1,058,037	Apr. 8, 1913	Collett, E.
1,058,145	do	Braun, F. W.
1,078,887	Nov. 18, 1913	Willson, T. L., *et al.*
1,083,429	Jan. 6, 1914	Brunschwig, F.
1,235,025	July 31, 1917	Glaeser, W.
1,246,636	Nov. 13, 1917	Meters, H. H.
1,251,741	Jan. 1, 1918	Blumenberg, H., Jr.
1,292,293	Jan. 21, 1919	Foss, A.
1,297,464	Mar. 18, 1919	Hechenbleikner, I.
1,313,379	Aug. 19, 1919	do
1,326,533	Dec. 30, 1919	Sadtler, S. S.
1,350,591	Aug. 24, 1920	Carothers, J. N.
1,383,990	July 5, 1921	Kelly, A.
1,428,259	Sept. 5, 1922	Rusberg, F.
1,447,544	Mar. 6, 1923	Glaser, W.
1,475,959	Dec. 4, 1923	Meyers, H. H.
1,485,406	Mar. 4, 1924	do
1,517,687	Dec. 2, 1924	Voerkelius, G. A.
1,530,397	Mar. 17, 1925	Oden, S. L. A., *et al.*
1,583,054	May 4, 1926	Klugh, B. G.
1,591,270	July 6, 1926	Blumenberg, H., Jr.
1,591,271	do	do
1,591,272	do	do
1,609,239	Nov. 30, 1926	do
1,753,478	Apr. 8, 1930	Pike, R. D.

<div align="center">TABLE 20—<i>Concluded</i></div>

Patent No.	Date	Patentee
1,786,097	Dec. 23, 1930	Thilo, E.
1,788,952	Jan. 13, 1931	Holz, August
1,806,029	May 19, 1931	Thorssell, C. T.
1,810,858	June 16, 1931	Thorssell, C. T., et al.
1,814,916	July 14, 1931	Haekl, H.
1,816,285	July 28, 1931	Johnson, E.
1,819,464	Aug. 18, 1931	Holz, A.
1,821,309	Sept. 1, 1931	Johnson, E.
1,821,653	do	Larsson, M.
1,821,859	do	Thorssell, T., et al.
1,833,680	Nov. 24, 1931	Kaselitz, O., et al.
1,834,454	Dec. 1, 1931	Johnson, E.
1,834,455	do	do
1,849,703	Mar. 15, 1932	Boller, E. R.
1,849,704	do	do
1,854,291	Apr. 18, 1932	Burdick, C. L.
1,856,187	May 3, 1932	Johnson, E.
1,857,296	May 10, 1932	Eyer, C., et al.
1,859,738	May 24, 1932	Johnson, E.
1,902,652	Mar. 21, 1933	Liljenroth, F. G.
1,903,684	Apr. 11, 1933	Palazzo, F. C., et al.
1,905,930	Apr. 25, 1933	McCallum, A. L., et al.
1,969,951	Aug. 14, 1933	Seyfried, W. R.
1,983,024	Dec. 4, 1934	Foss, A.
1,994,070	Mar. 12, 1935	do
2,036,244	Apr. 7, 1936	Wadsted, B., et al.
2,048,658	July 21, 1936	Jannek, T.
2,061,639	Nov. 24, 1936	Seyfried, W. R.
2,114,600	Apr. 19, 1938	Larsson, M.
2,134,013	Oct. 25, 1938	Turrentine, J. W.
2,143,438	Jan. 10, 1939	Fox, F. J.
2,170,843	Aug. 29, 1939	Turrentine, J. W.
2,173,825	Sept. 26, 1939	Curtis, H. A., et al.
2,173,826	do	do
2,211,918	Aug. 6, 1940	Turrentine, J. W.
2,252,280	Aug. 12, 1941	Balz, O., et al.
2,252,281	do	do
2,384,856	Sept. 18, 1945	Teneyck, H. S., et al.
2,504,446	Apr. 18, 1950	Plusje, M. H. R. J.

<div align="center">TABLE 21. U. S. PATENTS ON PHOSPHATES CONTAINING TWO OR MORE FERTILIZER INGREDIENTS</div>

Patent No.	Date	Patentee
16,111	Nov. 25, 1856	Bickell, C.
16,882	Mar. 24, 1857	Reid, L.
26,196	Nov. 22, 1859	Mapes, J. J.
34,825	Apr. 1, 1862	Gallacher, J. M.
35,417	May 27, 1862	Harper, L. McA.

TABLE 21—*Continued*

Patent No.	Date	Patentee
38,040	Mar. 31, 1863	Gale, L. D.
41,428	Feb. 2, 1864	Harper, L.
41,663	Feb. 16, 1864	Hayes, A. A.
49,891	Sept. 12, 1865	Klett, F.
61,870	Feb. 5, 1867	Reimer, F.
72,026	Dec. 10, 1867	Grimes, W. C.
75,336	Mar. 10, 1868	Wilson, G. F., *et al.*
77,840	May 12, 1868	Ramsburgh, J. S.
78,730	June 9, 1868	Fales, L. S.
88,443	Mar. 30, 1869	Burkholder, S. A., *et al.*
90,057	May 11, 1869	Stewart, D.
100,457	Mar. 1, 1870	Shepard, C. U., Jr.
100,729	Mar. 15, 1870	Commins, J.
110,084	Dec. 13, 1870	Spence, P.
113,416	Apr. 4, 1871	Forbes, D., *et al.*
124,964	Mar. 26, 1872	Manwaring, M. B., *et al.*
135,995	Feb. 18, 1873	McDougall, J.
173,621	May 20, 1875	Griffith, A. G.
206,077	July 16, 1878	Borkin, T. J., *et al.*
246,121	Aug. 23, 1881	Graf, L.
278,383	May 29, 1883	Young, J. R.
278,480	do	do
317,010	May 5, 1885	Pierce, W. S.
324,471	Aug. 18, 1885	Impeeratori, L.
345,625	July 13, 1886	Dunne, J. J.
353,210	Nov. 23, 1886	Dudley, D. W.
374,201	Dec. 6, 1887	Petraeus, C. V..
395,532	Jan. 1, 1889	Williams, W. J.
396,274	Jan. 15, 1889	Endemann, H.
404,348	May 28, 1889	do
407,240	July 16, 1889	Powter, N. B.
407,241	do	do
446,815	Feb. 17, 1891	Glaser, C.
446,998	Feb. 24, 1891	Van Ruymbeke, J.
450,253	Apr. 14, 1891	Reese, J.
450,254	do	do
450,255	do	do
450,531	do	do
453,749	June 9, 1891	Van Ruymbeke, J.
484,631	Oct. 18, 1892	Dunne, J. J.
494,940	Apr. 4, 1893	Rissmuller, L.
535,076	Mar. 5, 1895	Pieper, A. R. O.
601,089	Mar. 22, 1898	Wiborgh, J. G.
620,443	Feb. 28, 1899	Goldsmith, W. L.
703,295	June 24, 1902	Newport, R. B.
709,185	Sept. 16, 1902	Terne, B.
731,461	June 23, 1903	Jerecki, A. K.
897,695	Sept. 1, 1908	Young, J. R.

TABLE 21—*Continued*

Patent No.	Date	Patentee
911,283	Feb. 2, 1909	Young, J. R.
936,317	Oct. 12, 1909	Halvorsen, B. F.
988,894	Apr. 4, 1911	Peacock, S.
1,001,350	Aug. 22, 1911	Caro, N., *et al.*
1,011,909	Dec. 19, 1911	Brettville, A.
1,018,186	Feb. 20, 1912	Haff, M. M.
1,020,293	Mar. 12, 1912	Klingbiel, C.
1,036,909	Aug. 27, 1912	Saarbach, L.
1,040,081	Oct. 1, 1912	Willson, T. L., *et al.*
1,046,327	Dec. 3, 1912	Peacock, B.
1,057,876	Apr. 1, 1913	Peacock, S.
1,058,037	Apr. 8, 1913	Collett, E.
1,058,145	do	Braun, F. W.
1,058,249	Apr. 8, 1913	Meriwether, C. N.
1,062,869	May 27, 1913	Willson, T. L., *et al.*
1,099,151	June 2, 1914	Nicholas, F. C.
1,100,638	June 16, 1914	Washburn, F. S.
1,103,115	July 14, 1914	do
1,103,910	do	Willson, T. L., *et al.*
1,111,490	Sept. 22, 1914	Perino, J.
1,112,183	Sept. 29, 1914	Willson, T. L., *et al.*
1,115,044	Oct. 27, 1914	Washburn, F. S.
1,121,160	Dec. 15, 1914	Beckman, J. W.
1,122,183	Dec. 22, 1914	Willson, T. L., *et al.*
1,126,408	Jan. 26, 1915	Cowles, A. H.
1,127,840	Feb. 9, 1915	Willson, T. L., *et al.*
1,129,514	Feb. 23, 1915	Peacock, S.
1,129,722	do	do
1,142,068	June 8, 1915	Washburn, F. S.
1,144,405	June 29, 1915	Willson, T. L., *et al.*
1,145,107	July 6, 1915	do
1,146,222	July 13, 1915	do
1,149,390	Aug. 10, 1915	Meriwether, C. N.
1,150,899	Aug. 24, 1915	Strickler, E. H.
1,150,900	do	do
1,151,074	do	Washburn, F. S.
1,151,633	Aug. 31, 1915	do
1,161,473	Nov. 23, 1915	Haff, M. M., *et al.*
1,163,130	Dec. 7, 1915	Connor, J. H.
1,166,104	Dec. 28, 1915	Willson, T. L., *et al.*
1,167,788	Jan. 11, 1916	Washburn, F. S.
1,168,255	do	Herzka, E.
1,172,420	Feb. 22, 1916	Bassett, H. P.
1,194,077	Aug. 8, 1916	Ross, W. H., *et al.*
1,196,910	Sept. 5, 1916	Washburn, F. S.
1,208,877	Dec. 19, 1916	Wollenweber, W.
1,212,196	Jan. 16, 1917	Earp-Thomas, G. H.
1,214,346	Jan. 30, 1917	Messerschmitt, A.

TABLE 21—*Continued*

Patent No.	Date	Patentee
1,251,742	Jan. 1, 1918	Blumenberg, H., Jr.
1,252,318	do	do
1,258,106	Mar. 5, 1918	Gardiner, R. F., *et al.*
1,264,513	Apr. 30, 1918	Hechenbleikner, H.
1,264,514	do	do
1,272,001	July 9, 1918	Borghesani, G., *et al.*
1,275,276	Aug. 13, 1918	Lie, E.
1,276,555	Aug. 20, 1918	Meadows, T. C.
1,276,870	Aug. 27, 1918	Cameron, F. K.
1,280,650	Oct. 8, 1918	Bosch, C.
1,282,385	Oct. 22, 1918	Delacourt, A. F.
1,282,805	Oct. 29, 1918	Gardiner, R. F.
1,285,122	Nov. 19, 1918	Glaeser, W.
1,292,293	Jan. 21, 1919	Foss, A.
1,299,337	Apr. 1, 1919	Hechenbleikner, I.
1,310,080	July 5, 1919	Henwood, A.
1,350,591	Aug. 24, 1920	Carothers, J. N.
1,354,719	Oct. 5, 1920	Bohre, A. C.
1,355,369	Oct. 12, 1920	Washburn, F. S.
1,357,120	Oct. 26, 1920	Sadtler, S. S.
1,360,248	Nov. 23, 1920	Bobst, G. R.
1,360,401	Nov. 30, 1920	Hoffman, P. C.
1,360,402	do	do
1,366,569	Jan. 25, 1921	Kreiss, A. L.
1,367,846	Feb. 8, 1921	Washburn, F. S.
1,369,763	Feb. 22, 1921	Hetherington, H. C., *et al.*
1,377,553	May 10, 1921	Bloom, J. E.
1,411,696	Apr. 4, 1922	Haege, T.
1,413,013	Apr. 18, 1922	Edgar, G.
1,413,168	do	Kreiss, A. L.
1,413,048	do	Matheson, A.
1,417,248	May 23, 1922	Husson, J.
1,420,596	June 20, 1922	Webster, H. A.
1,428,259	Sept. 5, 1922	Rusberg, F.
1,440,056	Dec. 26, 1922	Clarkson, F., *et al.*
1,441,694	Jan. 9, 1923	McElroy, K. P.
1,456,850	May 29, 1923	Hazen, W., *et al.*
1,456,831	do	Ross, W. H., *et al.*
1,469,507	Oct. 2, 1923	Glaeser, W.
1,495,270	May 27, 1924	Stillsen, J. N. A.
1,510,179	Sept. 30, 1924	Liljenroth, F. G.
1,514,912	Nov. 11, 1924	Klugh, B. G.
1,517,687	Dec. 2, 1924	Voerkelius, G. A.
1,530,397	Mar. 17, 1925	Oden, S. L. A., *et al.*
1,542,986	June 23, 1925	Breslauer, J., *et al.*
1,588,651	June 15, 1926	Blumenberg, H., Jr.
1,591,270	July 6, 1926	do
1,591,271	do	do

TABLE 21—*Continued*

Patent No.	Date	Patentee
1,591,272	do	Blumenberg, H., Jr.
1,601,233	Sept. 28, 1926	do
1,610,109	Dec: 7, 1926	Peas, E. L., *et al.*
1,628,792	May 17, 1927	Larison, E. L., *et al.*
1,659,198	Feb. 14, 1928	Griessbach, R., *et al.*
1,699,393	Jan. 15, 1929	Hagens, J. F. C.
1,670,504	May 22, 1928	Griessbach, R., *et al.*
1,701,286	Feb. 5, 1929	Waggaman, W. H., *et al.*
1,716,415	June 11, 1929	Buchanan, G. H.
1,736,553	Nov. 19, 1929	Singleton, G., *et al.*
1,744,371	Jan. 21, 1930	Draisbach, F.
1,746,905	Feb. 11, 1930	Pike, R. D., *et al.*
1,758,448	May 13, 1930	Liljenroth, F. G.
1,760,990	June 3, 1930	Meyers, H. H.
1,761,400	do	Liljenroth, F. G.
1,768,075	June 24, 1930	Kipper, H. B.
1,790,503	Jan. 27, 1931	Hechenbleikner, I.
1,791,103	Feb. 3, 1931	Meyers, H. H.
1,799,479	Apr. 7, 1931	Pike, R. D.
1,805,873	May 19, 1931	Kaselitz, O.
1,806,029	do	Thorssell, C. T.
1,810,858	June 16, 1931	Thorssell, C. T., *et al.*
1,816,051	July 28, 1931	Lloyd, S. J., *et al.*
1,816,285	do	Johnson, E.
1,819,464	Aug. 18, 1931	Holz, A.
1,821,309	Sept. 1, 1931	Johnson, F.
1,821,653	do	Larsson, M.
1,822,040	Sept. 8, 1931	Klugh, B. G., *et al.*
1,826,785	Oct. 13, 1931	Holz, A.
1,834,418	Dec. 1, 1931	Pevere, E. P.
1,835,441	Dec. 8, 1931	Suchy, R., *et al.*
1,846,347	Feb. 23, 1932	Meyers, H. H.
1,855,856	Apr. 26, 1932	Hansen, C. J.
1,859,833	May 24, 1932	Mitteau, F.
1,865,968	July 5, 1932	Schuppe, W.
1,866,564	July 12, 1932	Hansen, C. J.
1,867,866	July 19, 1932	Ober, B., *et al.*
1,869,272	July 26, 1932	do
1,871,195	Aug. 9, 1932	do
1,873,490	Aug. 23, 1932	Schulze, R.
1,876,011	Sept. 6, 1932	Larsson, M.
1,878,426	Sept. 20, 1932	Pike, R. D.
1,878,997	Sept. 27, 1932	Adelantalo, L.
1,879,204	do	Guillissen, J.
1,884,105	Oct. 25, 1932	Moore, H. C.
1,884,751	do	Krase, H. J.
1,892,341	Dec. 27, 1932	Hackspill, L., *et al.*
1,913,539	June 13, 1933	Friedrich, H.

TABLE 21—*Concluded*

Patent No.	Date	Patentee
1,913,791	June 13, 1933	Carothers, J. N.
1,916,429	July 4, 1933	Larsson, M.
1,939,351	Dec. 12, 1933	Johnson, E.
1,945,914	Feb. 6, 1934	Reubke, E.
1,949,129	Feb. 27, 1934	Oehme, H.
1,960,030	May 22, 1934	Sackett, A. J.
1,969,894	Aug. 14, 1934	Liljenroth, F. G.
1,998,631	Apr. 23, 1935	Tramm, H., *et al.*
1,999,026	Apr. 23, 1935	do
2,019,713	Nov. 5, 1935	Lawrence, C. K.
2,022,050	Nov. 26, 1935	Levermore, C. H.
2,037,706	Apr. 21, 1936	Curtis, H. A.
2,040,563	May 12, 1936	Phillips, J. J.
2,053,432	Sept. 8, 1936	Harvey, E. W.
2,069,226	Feb. 2, 1937	Curtis, H. A.
2,070,581	Feb. 16, 1937	do
2,070,658	do	Hartenstein, H. L.
2,077,171	Apr. 13, 1937	Harvey, E. W., *et al.*
2,081,401	May 25, 1937	Kniskern, W. H., *et al.*
2,083,652	June 15, 1937	Kaselitz, O.
2,086,717	July 13, 1937	Kniskern, W. H., *et al.*
2,086,912	do	Kaselitz, O.
2,092,123	Sept. 7, 1937	do
2,102,830	Dec. 21, 1937	Brill, J. L.
2,102,831	do	do
2,104,295	Jan. 4, 1938	De Varda, G.
2,130,483	Sept. 20, 1938	Bull, B. A.
2,135,545	Nov. 8, 1938	Boelkel, W.
2,142,965	Jan. 3, 1939	Hale, W. J.
2,149,966	Mar. 7, 1939	Kniskern, W. H., *et al.*
2,288,418	June 30, 1942	Partridge, E. P.
2,348,343	Mar. 9, 1944	Holbrook, J. C.
2,366,857	Jan. 9, 1945	Hurka, R. J.
2,434,899	Jan. 27, 1948	Biggs, J. D.
2,439,432	Apr. 13, 1948	Keenan, F. G. and Dodge, R. L.
2,504,545	Apr. 18, 1950	Waring, C. E., *et al.*

TABLE 22. U. S. PATENTS ON GRANULATION AND CONDITIONING OF MANUFACTURED PHOSPHATES

Patent No.	Date	Patentee
75,328	Mar. 10, 1868	Wilson, G. F.
75,330	do	do
75,331	do	do
75,333	do	do
75,334	do	do
75,337	do	do
102,648	May 3, 1870	Baugh, E. P.
106,147	Aug. 9, 1870	Frank, E., *et al.*

TABLE 22—*Continued*

Patent No.	Date	Patentee
496,687	May 2, 1893	Huffman, P. C.
1,036,896	Aug. 27, 1912	Peacock, S.
1,151,633	Aug. 31, 1915	Washburn, F. S.
1,161,473	Nov. 23, 1915	Haff, M. M., *et al.*
1,418,618	June 6, 1922	Butt, C. A.
1,430,621	Oct. 3, 1922	Bruhn, G. A.
1,439,054	Dec. 19, 1922	Armstrong, E. H.
1,485,406	Mar. 4, 1924	Meyers, H. H.
1,551,152	Aug. 25, 1925	Hiller, S.
1,567,408	Dec. 29, 1925	Axelsen, P. T.
1,573,533	Feb. 16, 1926	Barr, J. A.
1,606,004	Nov. 9, 1926	Tyler, A. W.
1,628,481	May 10, 1927	Vernay, J. B.
1,645,373	Oct. 11, 1927	Couch, D. H.
1,653,332	Dec. 20, 1927	Baechler, M.
1,681,690	Aug. 21, 1928	Vernay, J. B.
1,689,697	Oct. 30, 1928	Thornton, E. W.
1,695,193	Dec. 11, 1928	Krall, R. T.
1,715,729	June 4, 1929	Washington, D. E.
1,718,104	June 18, 1929	Baechler, M.
1,756,835	Apr. 29, 1930	Sackett, A. J.
1,782,038	Nov. 18, 1930	Haak, B.
1,782,054	do	Uhl, B. F.
1,782,822	Nov. 25, 1930	Hechenbleikner, I.
1,790,502	Jan. 27, 1931	do
1,790,503	do	do
1,808,626	June 2, 1931	Bechtel, G. M.
1,818,114	Aug. 11, 1931	Carothers, J. N., *et al.*
1,824,717	Sept. 22, 1931	Harty, W. A., *et al.*
1,837,283	Dec. 22, 1931	Ober, B., *et al.*
1,837,284	do	do
1,837,304	do	Wight, E. H.
1,837,305	do	Wight, E. H., *et al.*
1,837,307	do	do
1,837,328	do	Ober, B., *et al.*
1,837,329	do	do
1,837,331	do	do
1,837,332	do	do
1,847,543	Mar. 1, 1932	Warming, K.
1,860,738	May 31, 1932	Harty, W. A., *et al.*
1,865,383	June 28, 1932	Ober, B., *et al.*
1,867,866	July 19, 1932	do
1,869,272	July 26, 1932	do
1,869,941	Aug. 2, 1932	do
1,869,952	do	Anderson, D. L.
1,871,895	Aug. 16, 1932	Luscher, E.
1,875,879	Sept. 6, 1932	McKee, R. H.
1,888,919	Nov. 22, 1932	Gooch, S. D.
2,040,081	May 12, 1936	Curtis, H. A.

TABLE 22—*Concluded*

Patent No.	Date	Patentee
2,072,980	Mar. 9, 1937	Curtis, H. A.
2,136,793	Nov. 15, 1938	Gabeler, W. C., *et al.*
2,181,933	Dec. 5, 1939	Block, L., *et al.*
2,182,613	do	Fiske, A. H.
2,198,592	Apr. 30, 1940	Hagood, J.
2,287,759	June 23, 1942	Hardesty, J. O., *et al.*
2,304,382	Dec. 8, 1942	Shoeld, M.
2,308,220	Jan. 12, 1943	Waggaman, W. H.
2,442,513	Jan. 1, 1948	Sackett, W. J.
2,504,545	Apr. 18, 1950	Waring, C. E., *et al.*

TABLE 23. U. S. PATENTS ON THE MANUFACTURE OF DICALCIUM PHOSPHATE

Patent No.	Date	Patentee
418,259	Dec. 31, 1889	Winssinger, C. E. D.
462,366	Nov. 3, 1891	Simpson, J.
690,048	Dec. 31, 1901	Cheeseman, L.
690,049	do	do
707,886	Aug. 26, 1902	Wiburgh, J. G., *et al.*
736,730	Aug. 18, 1903	Huyerman, G.
748,523	1903	Palmaer, W.
789,647	May 9, 1905	Avens, R.
819,410	May 1, 1906	Clemm, A.
852,371	Apr. 30, 1907	Bergmann, E.
852,372	do	do
995,894	June 20, 1911	Palmaer, W.
1,020,153	Mar. 12, 1912	Newberry, S. B., *et al.*
1,057,876	Apr. 1, 1913	Peacock, S.
1,326,533	Dec. 30, 1919	Sadtler, S. S.
1,348,495	Aug. 3, 1920	James, C. C.
1,699,393	Jan. 15, 1929	Hagens, J. F. C.
1,753,478	Apr. 8, 1930	Pike, R. D.
1,786,097	Dec. 23, 1930	Thilo, E.
1,788,952	Jan. 13, 1931	Holz, A.
1,819,464	Aug. 18, 1931	do
1,826,785	Oct. 13, 1931	do
1,851,210	Mar. 29, 1932	Palazzo, F. C., *et al.*
1,876,501	Sept. 6, 1932	Johnson, E.
1,969,951	Aug. 14, 1934	Seyfried, W. R.
2,021,527	Nov. 19, 1935	Suehy, R., *et al.*
2,043,238	June 9, 1936	Curtis, H. A.
2,078,627	Apr. 27, 1937	Block, L & Melziger, M.
2,086,912	July 13, 1937	Kaselitz, O.
2,108,940	Feb. 23, 1938	MacIntire, W. H.
2,114,600	Apr. 19, 1938	Larsson, M.
2,115,150	Apr. 26, 1938	Seyfried, W. R.
2,287,699	June 23, 1942	Moss, H. V., *et al.*
2,287,758	do	Fox, E. J.
2,296,494	Sept. 22, 1942	Block, E.
2,353,658	July 18, 1944	Fox, E. J.

TABLE 24. U. S. PATENTS ON THE CALCINATION AND FUSION OF
PHOSPHATE ROCK WITH SILICA, AN ALKALI OR AN ALKALINE
EARTH COMPOUND

Patent No.	Date	Patentee
45,961	Jan. 17, 1865	Liebig, G. A., *et al.*
49,891	Sept. 12, 1865	Klett, F.
74,799	Feb. 25, 1868	Commins, J.
78,061	May 19, 1868	do
102,438	Apr. 26, 1870	Sapp, W. I.
119,994	Oct. 17, 1871	Prescott, D. W.
252,029	Jan. 25, 1882	Gibbons, J. F., *et al.*
284,674	Sept. 11, 1883	Rocour, G.
345,652	July 13, 1886	Dunne, J. J.
453,299	June 2, 1891	Glaser, C.
453,300	do	do
542,080	July 2, 1895	Day, D. T.
588,266	Aug. 17, 1897	DeChalmot, G.
589,197	Aug. 31, 1897	Stead, J. E.
598,182	Feb. 1, 1898	Poole, H.
601,089	Mar. 22, 1898	Wiborgh, J. G.
721,489	Feb. 24, 1903	Wolters, W.
917,502	Apr. 6, 1909	Strickler, E. H.
922,494	May 25, 1909	Lowman, J. W.
931,846	Aug. 24, 1909	Connor, J. H.
972,567	Oct. 24, 1910	Newberry, S. B.
978,193	Dec. 13, 1910	do
991,096	May 2, 1911	Schroder, H.
1,002,198	Aug. 29, 1911	Freirichs, F. W.
1,016,352	Feb. 6, 1912	Meriwether, C. N.
1,016,989	Feb. 13, 1912	Galt, H. A.
1,025,619	May 7, 1912	Giese, F., *et al.*
1,042,400	Oct. 29, 1912	Connor, J. H.
1,042,401	do	do
1,042,402	do	do
1,042,588	do	Newberry, S. B., *et al.*
1,046,327	Dec. 3, 1912	Peacock, B.
1,058,249	Apr. 8, 1913	Meriweather, C. N.
1,074,779	Oct. 7, 1913	Dunham, H. V.
1,074,808	do	Newberry, S. B., *et al.*
1,076,200	Oct. 21, 1913	Dunham, H. V.
1,094,857	Apr. 28, 1914	Landis, W. S.
1,099,151	June 2, 1914	Nicholas, T. C.
1,103,059	July 14, 1914	Landis, W. S.
1,103,910	do	Wilson, T. L., *et al.*
1,111,490	Sept. 22, 1914	Perine, J.
1,120,917	Dec. 15, 1914	Downs, W. F.
1,121,160	do	Beckman, J. W.
1,126,408	Jan. 26, 1915	Gowles, A. H.
1,137,065	Apr. 27, 1915	Landis, W. S.
1,144,405	June 29, 1915	Wilson, T. L., *et al.*
1,149,390	Aug. 10, 1915	Meriwether, C. N.

TABLE 24—*Continued*

Patent No.	Date	Patentee
1,158,711	Nov. 2, 1915	Newberry, S. B., *et al.*
1,162,802	Dec. 7, 1915	do
1,162,944	do	do
1,163,130	do	Connor, J. H.
1,172,420	Feb. 22, 1916	Newberry, S. B., *et al.*
1,173,303	Feb. 29, 1916	do
1,174,176	Mar. 7, 1916	do
1,194,219	Aug. 8, 1916	do
1,204,238	Nov. 7, 1916	Bishop, E. S.
1,214,008	Jan. 30, 1917	Ciselet, E., *et al.*
1,214,346	do	Messerschmitt, A.
1,229,684	June 12, 1917	Volpato, V.
1,236,812	Aug. 14, 1917	Zilk, J. E.
1,247,059	Nov. 20, 1917	do
1,251,742	Jan. 1, 1918	Blumenberg, H., Jr.
1,252,318	do	Blumenberg, H., Jr.
1,258,106	Mar. 5, 1918	Gardiner, R. F.
1,267,473	May 28, 1918	Stoppani, E., *et al.*
1,272,001	July 9, 1918	Borghesani, G., *et al.*
1,281,681	Oct. 15, 1918	Soper, E. C.
1,282,385	Oct. 22, 1918	Delacourt, A. F.
1,282,805	Oct. 29, 1918	Gardiner, R. F.
1,285,122	do	Glaeser, W.
1,293,220	Feb. 4, 1919	Shuey, P. MacG.
1,310,080	July 15, 1919	Henwood, A.
1,360,248	Nov. 23, 1920	Brobst, G. R.
1,366,569	Jan. 25, 1921	Kreiss, A. L.
1,372,051	Mar. 22, 1921	Tromp, F. J.
1,379,735	May 31, 1921	Walker, G. T.
1,387,151	Aug. 9, 1921	Glaeser, W.
1,393,839	Oct. 18, 1921	Shoeld, M.
1,393,840	do	do
1,396,149	Nov. 8, 1921	Soper, E. C.
1,396,975	Nov. 15, 1921	do
1,411,696	Apr. 4, 1922	Haege, T.
1,413,168	Apr. 18, 1922	Kreiss, A. L.
1,437,456	Dec. 5, 1922	Soper, E. C.
1,578,339	Mar. 30, 1926	Meyers, H. H.
1,696,975	Jan. 1, 1929	Rothe, F., *et al.*
1,704,218	Mar. 5, 1929	do
1,795,173	Mar. 3, 1931	Lehrecke, H.
1,799,882	Apr. 7, 1931	Brenek, H.
1,810,402	June 16, 1931	Rothe, F., *et al.*
1,845,876	Feb. 16, 1932	Huber, H.
1,846,347	Feb. 23, 1932	Meyers, H.
1,854,765	Apr. 19, 1932	Rothe, F., *et al.*
1,855,190	Apr. 26, 1932	Kern, L.
1,878,185	Sept. 20, 1932	Rothe, F., *et al.*
1,902,832	May 28, 1933	Caldwell, P.

TABLE 24—*Concluded*

Patent No.	Date	Patentee
1,880,491	Oct. 4, 1932	Rothe, F., *et al.*
1,994,070	Mar. 12, 1935	Foss, A.
2,044,774	June 23, 1936	Curtis, H. A.
2,070,697	Feb. 16, 1937	Tromel, G.
2,093,176	Sept. 14, 1937	do
2,121,776	June 28, 1938	Baily, T. F.
2,143,865	Jan. 17, 1939	Copson, R. L.
2,155,556	Apr. 25, 1939	Kerschbaum, F. P.
2,165,729	July 11, 1939	Rusberg, F.
2,183,379	Dec. 12, 1939	Franck, H., *et al.*
2,189,248	Feb. 6, 1940	Luscher, E.
2,220,575	Nov. 5, 1940	do
2,222,740	Nov. 26, 1940	Bornemann, F., *et al.*
2,230,539	Feb. 4, 1941	Johannsen, O., *et al.*
2,288,112	June 30, 1942	Shoeld, M.
2,337,498	Dec. 21, 1943	Ritter, F., *et al.*
2,368,649	Feb. 6, 1945	Elmore, K. L.
2,395,219	Feb. 19, 1946	Gooch, S. D.
2,442,969	June 8, 1948	Butt, C. A.
2,446,978	Aug. 10, 1948	Maust, E. J.
2,478,200	Aug. 9, 1949	Maust, E. J., *et al.*
2,479,389	Aug. 16, 1949	do
2,499,385	Mar. 7, 1950	Hubbuch, T. N., *et al.*
2,499,767	do	Maust, E. J.
2,531,046	Nov. 21, 1950	Hollingsworth, C. R.
2,531,068	do	Maust, E. J.

TABLE 25. U. S. PATENTS ON THE MANUFACTURE OF METAPHOSPHATES, PYROPHOSPHATES AND POLYPHOSPHATES

Patent No.	Date	Patentee
446,087	Feb. 10, 1891	Van Ruymbeke, J.
446,998	Feb. 24, 1891	do
502,424	Aug. 1, 1893	Precht, H.
995,028	June 13, 1911	Newberry, S. B., *et al.*
1,002,143	Aug. 29, 1911	Frerichs, F. W.
1,002,198	do	do
1,034,090	July 30, 1912	Dunham, H. V.
1,078,887	Nov. 18, 1913	Willson, T. L., *et al.*
1,194,077	Aug. 8, 1916	Ross, W. H., *et al.*
1,383,990	July 5, 1921	Kelly, A.
1,438,588	Dec. 12, 1922	Feldenheimer, Wm.
1,447,544	Mar. 6, 1923	Glaser, W.
1,654,283	Dec. 27, 1927	Dickerson, W. H.
1,654,404	do	Blumenberg, H., Jr.
1,699,093	Jan. 15, 1929	Carothers, J. N., *et al.*
1,747,579	Feb. 18, 1930	Durgin, C. G., *et al.*
1,837,230	Dec. 22, 1931	Miner, C. G.
1,897,892	Feb. 14, 1933	Draisbach, F.

Table 25—*Continued*

Patent No.	Date	Patentee
1,903,041	Mar. 28, 1933	Hall, R. E., *et al.*
1,956,515	Apr. 24, 1934	Hall, R. E.
1,979,926	Nov. 6, 1934	Zinn, R. E.
1,991,850	Feb. 19, 1935	Hall, R. E.
1,997,256.	Apr. 9, 1935	do
2,008,651	July 16, 1935	Zinn, R. E.
2,009,692	July 30, 1935	Hall, R. E.
2,019,142	Oct. 29, 1935	Kuever, R. A.
2,019,665	Nov. 5, 1935	Fiske, A. H., *et al.*
2,019,666·	do	do
2,024,543	Dec. 17, 1935	Smith, G. W.
2,025,503	Dec. 24, 1935	Fiske, A. H.
2,031,827	Feb. 25, 1936	do
2,033,913	Mar. 17, 1936	do
2,035,652	Mar. 31, 1936	Hall, R. E.
2,038,316	Apr. 21, 1936	Rosenstein, L.
2,041,448	May 19, 1936	Zinn, R. E.
2,055,332	Sept. 22, 1936	Bryan, C. S.
2,059,570	Nov. 3, 1936	Fiske, A. H.
2,063,788	Dec. 8, 1936	Burk, R. E.
2,064,110	Dec. 15, 1936	Hall, R. E.
2,064,387	do	Schwartz, C.
2,067,628	Jan. 12, 1937	Fiske, A. H.
2,071,385	Feb. 23, 1937	Bell, E. B.
2,075,653	Mar. 30, 1937	Libbey, A. G.
2,078,071	Apr. 20, 1937	Fiske, A. H.
2,078,943	May 4, 1937	Hall, R. E.
2,081,273	May 25, 1937	Hoermann, F., *et al.*
2,081,617	May 25, 1937	Draisbach, F.
2,082,573	June 1, 1937	Hall, R. E.
2,086,309	July 6, 1937	Wharton, J.
2,086,867	July 13, 1937	Hall, R. E.
2,087,089	do	do
2,087,849	July 20, 1937	Wilson, J. A.
2,092,913	Sept. 14, 1937	Fiske, A. H.
2,097,517	Nov. 2, 1937	Durgin, C. G.
2,098,431	Nov. 9, 1937	Partridge, E. P.
2,105,446	Jan. 11, 1938	Wilson, J. A.
2,107,857	Feb. 8, 1938	Emmett, P. H.
2,108,553	Feb. 15, 1938	Speas, V. E., *et al.*
2,108,563	do	do
2,108,783	Feb. 15, 1938	Smith, G. W.
2,110,010	Mar. 1, 1938	White, C. E., *et al.*
2,110,870	Mar. 15, 1938	Curtis, H. A., *et al.*
2,113,574	Apr. 12, 1935	do
2,114,599	Apr. 19, 1938	Jones, K. K.
2,128,160	Aug. 23, 1938	Morgan, L. C.
2,128,161	Aug. 23, 1938	do

TABLE 25—*Concluded*

Patent No.	Date	Patentee
2,134,346	Oct. 25, 1938	Siefert, F.
2,135,054	Nov. 1, 1938	Schwartz, C.
2,141,189	Dec. 27, 1938	Lyons, S. C.
2,145,344	Jan. 31, 1939	Draisbach, F.
2,149,734	Mar. 7, 1939	Hall, R. E.
2,150,060	do	Guttenberg, F. H. Von
2,163,065	June 20, 1939	Rosenstein, L.
2,164,092	June 27, 1939	Smith, G. W.
2,167,327	July 25, 1939	Talley, S. K.
2,172,216	Sept. 5, 1939	Miller, A.
2,173,825	Sept. 26, 1939	Curtis, H. A., *et al.*
2,173,826	do	do
2,174,614	Oct. 3, 1939	Bornemann, F., *et al.*
2,180,742	Nov. 21, 1939	Lyons, S. C.
2,182,045	Dec. 5, 1939	Bell, E. B.
2,184,287	Dec. 26, 1939	Curtis, H. A., *et al.*
2,191,199	Feb. 20, 1940	Hall, R. E.
2,191,206	do	Schwartz, C.
2,196,300	Apr. 9, 1940	Grettie, D. P.
2,209,129	July 23, 1940	Mengele, H., *et al.*
2,211,688	Aug. 13, 1940	Byck, H. T., *et al.*
2,215,137	do	Schwartz, C.
2,215,814	Sept. 24, 1940	Hall, R. E.
2,216,207	Oct. 1, 1940	Menaul, P. L.
2,223,316	Nov. 26, 1940	Ellis, C., *et al.*
2,228,133	Jan. 7, 1941	Breach, A. M.
2,233,401	Mar. 1, 1941	Copson, R. L.
2,233,973	do	Dunn, T. H.
2,233,974	Mar. 1, 1941	do
2,239,284	Apr. 22, 1941	Draisbach, F.
2,241,868	May 13, 1941	Reimann, A.
2,244,158	June 3, 1941	Hubbard, F. E., *et al.*
2,266,486	Dec. 16, 1941	Booth, C. F.
2,296,716	Sept. 22, 1942	Jelen, F. C.
2,360,730	Oct. 17, 1944	Smith, G. W.
2,369,407	Feb. 13, 1945	Robinson, W. W., Jr.
2,393,560	Jan. 22, 1946	Partridge, E. P.
2,413,159	Dec. 24, 1946	Weyl, W. A.
2,414,742	Jan. 21, 1947	Jackson, H. A.
2,417,344	Mar. 11, 1947	Barrett, G. R.
2,418,525	Apr. 8, 1947	Pollak, F. F.
2,419,147	Apr. 15, 1947	King, C. S.
2,419,148	do	do
2,427,847	Sept. 23, 1947	Fryling, C. F.
2,437,297	May 9, 1948	Garrison, A. D.
2,477,492	July 26, 1949	Moose, J. E.
2,511,249	June 13, 1950	Durgin, C. B., *et al.*

TABLE 26. U. S. PATENTS ON THE MANUFACTURE OF ALKALI
METAL PHOSPHATES

Patent No.	Date	Patentee
123,743	Feb. 13, 1872	Tanner, B.
284,674	Sept. 11, 1883	Rocour, G.
301,407	July 1, 1884	Thomas, S. G.
324,471	Aug. 18, 1885	Imperatori, L.
361,656	Apr. 19, 1887	Twynam, T.
446,815	Feb. 17, 1891	Glaser, C.
502,424	Aug. 1, 1893	Precht, H.
504,453	Sept. 5, 1893	Meyer, T.
598,182	Feb. 1, 1898	Poole, H.
950,159	Feb. 22, 1910	Ridenour, W. E.
1,037,837	Sept. 3, 1912	Strickler, E. H.
1,046,327	Dec. 3, 1912	Peacock, B.
1,372,051	Mar. 22, 1921	Tromp, F. J.
1,379,735	May 21, 1921	Walker, G. T.
1,447,554	May 21, 1923	Glaeser, W.
1,504,339	Aug. 12, 1924	do
1,504,340	do	do
1,572,846	Feb. 9, 1926	Hoff, C. M.
1,638,677	Aug. 9, 1927	Blumenberg, H., Jr.
1,642,244	Sept. 13, 1927	Howard, H.
1,644,161	Oct. 4, 1927	Walker, G. T.
1,648,656	Nov. 8, 1927	Meyers, H. H.
1,654,283	Dec. 27, 1927	Dickerson, W. H.
1,654,404	do	Blumenberg, H., Jr.
1,676,556	July 10, 1928	Howard, H.
1,686,673	Oct. 9, 1928	Miner, C. G.
1,686,835	do	Pike, R. D., *et al.*
1,686,836	do	do
1,688,112	Oct. 16, 1928	Booth, C. F., *et al.*
1,689,547	Oct. 30, 1928	Carothers, J. N.
1,699,093	Jan. 15, 1929	Carothers, J. N., *et al.*
1,700,972	Feb. 5, 1929	Booth, C. F., *et al.*
1,700,973	do	do
1,711,707	May 7, 1929	West-brook, L. R.
1,727,551	Sept. 10, 1929	Lohmann, W. H.
1,744,371	Jan. 21, 1930	Draisbach, F.
1,746,905	Feb. 11, 1930	Pike, R. D., *et al.*
1,746,906	do	do
1,747,588	Feb. 18, 1930	Lohmann, W. H.
1,759,152	May 20, 1930	Booth, C. F., *et al.*
1,760,990	June 3, 1930	Meyers, H. H.
1,768,075	June 24, 1930	Kipper, H. B.
1,790,502	Jan. 27, 1931	Hechenbleikner, I.
1,791,103	Feb. 3, 1931	Meyers, H. H.
1,799,479	Apr. 7, 1931	Pike, R. D.
1,805,873	May 19, 1931	Kaselitz, O.

TABLE 26—*Continued*

Patent No.	Date	Patentee
1,807,766	June 2, 1931	Conway, B. Von G., *et al.*
1,816,051	July 28, 1931	Lloyd, S. J., *et al.*
1,817,858	Aug. 4, 1931	Ulman, F., *et al.*
1,825,965	Oct. 6, 1931	Lang, P. A.
1,845,876	Feb. 16, 1932	Huber, H.
1,846,347	Feb. 23, 1932	Meyers, H. H.
1,855,856	Apr. 26, 1932	Hanson, C. J.
1,859,833	May 24, 1932	Mitteau, F.
1,860,818	May 31, 1932	Rohre, K., *et al.*
1,865,588	July 5, 1932	Reimann, A.
1,865,968	do	Schuppe, W.
1,866,657	July 12, 1932	Levermore, C. L.
1,873,490	Aug. 23, 1932	Schulze, R.
1,876,426	Sept. 20, 1932	Pike, R. D.
1,876,997	do	Adelantalo, L.
1,878,426	Sept. 20, 1932	Pike, R. D.
1,883,447	Oct. 18, 1932	Ammen, T. G.
1,885,905	Nov. 1, 1932	Frost, F. L., Jr.
1,887,445	Nov. 8, 1932	Conway, B. von G., *et al.*
1,888,003	Nov. 15, 1932	Lindberg, N. C.
1,890,453	Dec. 13, 1932	Bowman, F. C.
1,891,293	Dec. 20, 1932	Girsewald, C., *et al.*
1,892,341	Dec. 27, 1932	Hackspill, L., *et al.*
1,897,705	Feb. 14, 1933	Mandlen, H.
1,901,020	Mar. 14, 1933	Booth, C. F.
1,903,582	Apr. 11, 1933	Conway, B. von G., *et al.*
1,913,796	June 13, 1933	Deutman, F. R.
1,926,747	Sept. 12, 1933	Lindberg, N. C., *et al.*
2,031,827	Feb. 25, 1936	Fiske, A. H., *et al.*
2,033,913	Mar. 17, 1936	do
2,064,979	Dec. 22, 1936	Kaselitz, O.
2,109,811	Mar. 1, 1938	Welter, A.
2,142,943	Jan. 3, 1939	Kerschbaum, F. P.
2,142,944	do	do
2,162,657	June 13, 1939	Wehrstein, A.
2,165,948	July 11, 1939	Taylor, E. A.
2,187,536	Jan. 16, 1940	Avedikian, S. Z.
2,204,357	June 11, 1940	Heckert, W. W.
2,204,358	do	do
2;204,364	do	Kepfer, R. J.
2,220,790	Nov. 5, 1940	McCullough, C. R.
2,221,356	Nov. 12, 1940	Michels, A.
2,266,328	Dec. 16, 1941	McCullough, C. R.
2,271,712	Feb. 3, 1942	Peirce, G. A.
2,280,848	Apr. 28, 1942	Pole, G. R.
2,349,943	May 30, 1944	Ditzel, A. C.
2,358,965	Sept. 26, 1944	Durgin, C. B., *et al.*
2,375,054	May 1, 1945	Waddell, M. C.
2,385,188	Sept. 18, 1945	Booth, C. F.

TABLE 26—*Concluded*

Patent No.	Date	Patentee
2,387,746	Sept. 25, 1945	Colton, H. S., *et al.*
2,395,219	Feb. 19, 1946	Gooch, S. D.
2,408,258	Sept. 24, 1946	Hetzel, E. N., *et al.*
2,419,147	Apr. 15, 1947	King, C. S.
2,419,148	do	do
2,423,154	July 1, 1947	O'Brien, J. W.
2,436,670	Feb. 24, 1948	Russell, C. H.
2,468,448	Apr. 26, 1949	King, C. S.
2,468,455	do	Metziger, M.
2,484,266	Oct. 11, 1949	Bowe, L. E.

TABLE 27. U. S. PATENTS RELATED TO PHOSPHATE LEAVENING
AGENTS AND BAKING PREPARATIONS[1]

Patent No.	Date	Patentee
14,722	Apr. 22, 1856	Horsford, E.
41,815	Mar. 1, 1864	do
42,140	Mar. 29, 1864	do
62,277	Mar. 29, 1867	Laur, J.
75,271	Mar. 10, 1868	Horsford, E.
75,272	do	do
75,325	do	Wilson, G.
75,326	do	do
75,327	do	do
75,328	do	do
75,329	do	do
75,330	do	do
75,336	do	Wilson, G., and Horsford, E.
75,337	do	do
75,338	do	do
75,339	do	do
76,763	do	Horsford, E.
104,035	June 7, 1870	do
110,680	Jan. 3, 1871	Rice, N. B.
118,768	Sept. 6, 1871	Wilson, G.
130,298	Aug. 6, 1872	Horsford, E.
140,251	Aug. 6, 1873	Lauer, J.
143,580	Oct. 14, 1873	Copping, J. G., *et al.*
178,146	May 30, 1876	Hecker, J.
196,771	Nov. 6, 1877	Seibel, J.
196,881	do	Designolle, P.
224,998	Mar. 2, 1880	Dart, H.
229,518	July 6, 1880	Catlin, C.
229,573	do	Wilson, G.
229,574	do	do
229,705	do	Horsford, E.
230,874	Aug. 10, 1880	do
256,832	Apr. 25, 1882	Giesecke, A.

[1] Prepared by H. W. Easterwood, Victor Chemical Works.

TABLE 27—*Continued*

Patent No.	Date	Patentee
269,743	Dec. 26, 1882	Thorpe, P.
301,407	July 1, 1884	Thomas, S. G.
315,831	Apr. 14, 1885	Peters, A.
331,542	Dec. 1, 1885	do
439,267	Oct. 28, 1890	Catlin, C.
474,811	May 17, 1892	do
654,570	July 24, 1900	Hunt, P.
654,571	do	Hunt, P.
654,572	do	do
654,573	do	do
657,334	Sept. 4, 1900	Clotworthy, W.
673,057	Apr. 30, 1901	Kochs, A.
674,140	May 14, 1901	Patten, W.
692,451	Feb. 4, 1902	Just, J.
692,452	do	do
884,606	Apr. 14, 1908	McFarland, R.
983,719	Feb. 7, 1911	Humphries, H.
990,699	Apr. 25, 1911	Brown, W. B. and Holbrook, R
1,063,177	June 3, 1913	Andrews, W. G.
1,113,632	Oct. 13, 1914	Holbrook, R.
1,150,900	Aug. 24, 1915	Strickler, E.
1,150,901	do	do
1,158,933	Nov. 2, 1915	Kohman, H., *et al.*
1,158,934	do	do
1,210,940	Jan. 2, 1917	Holbrook, R.
1,234,858	July 31, 1917	Blacklock, T.
1,264,592	Apr. 30, 1918	Atkinson, F.
1,286,904	Dec. 10, 1918	do
1,356,988	Oct. 26, 1920	Johns, C., *et al.*
1,370,272	Mar. 1, 1921	Blinn, H.
1,427,979	Sept. 5, 1922	Stokes, W.
1,431,156	Oct. 10, 1922	Geere, W., *et al.*
1,442,318	Jan. 16, 1923	Whittier, C.
1,447,054	Feb. 27, 1923	Warner, F.
1,497,477	June 10, 1924	Blouch, L., and Roop, J.
1,500,545	July 8, 1924	Buffington, L.
1,538,910	May 26, 1925	Stokes, W.
1,558,888	Oct. 27, 1925	Jones, R. E.
1,599,563	Sept. 14, 1926	Fiske, A.
1,630,143	May 24, 1927	Sullivan, E. J.
1,643,011	Sept. 20, 1927	Hill, C. and Tintner, G.
1,643,012	do	do
1,657,116	Jan. 24, 1928	Fiske, A.
1,689,697	Oct 20, 1928	Thornton, E.
1,699,093	Jan. 15, 1929	Carothers, J. and Booth, C.
1,702,259	Feb. 19, 1929	Hill, C. B., *et al.*
1,712,025	May 7, 1929	Brown, O.
1,758,920	May 20, 1930	Baum, G.
1,775,037	Sept. 2, 1930	Fiske, A.

<div align="center">

TABLE 27—*Continued*

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Patent No.	Date	Patentee
1,785,473	Dec. 16, 1930	Adler, H. and McDonald, G.
1,787,193	Dec. 30, 1930	Fiske, A.
1,790,502	Jan. 27, 1931	Hechenbleikner, I.
1,803,588	May 5, 1931	Black, A., *et al.*
1,808,108	June 2, 1931	Hawks, J.
1,818,114	Aug. 11, 1931	Carothers, J. and Logue, P.
1,831,728	Nov. 10, 1931	Working, E.
1,834,747	Dec. 1, 1931	Stokes, W.
1,841,944	Jan. 19, 1932	Geere, E.
1,843,051	Jan. 26, 1932	Thiele, F.
1,847,799	Mar. 1, 1932	Weil, L.
1,859,250	May 17, 1932	Bertel, R.
1,907,764	May 9, 1933	Epstein, A. and Harris, B.
1,913,796	June 13, 1933	Deutman, F.
1,924,137	Aug. 29, 1933	Stokes, W. and Whittier, C.
1,926,572	Sept. 12, 1933	Wight, E.
1,936,636	Nov. 28, 1933	MacIntosh, C. H.
1,943,919	Jan. 16, 1934	Knox, W., Jr.
1,951,328	Mar. 13, 1934	Fiske, A.
1,952,947	Mar. 27, 1934	Schott, C.
1,984,968	Dec. 18, 1934	Fiske, A. and Bryan C.
2,012,436	Aug. 27, 1935	Saklatwalla, B., *et al.*
2,018,449	Oct. 22, 1935	Knox, W., Jr.
2,021,012	Nov. 12, 1935	McCullough, C.
2,036,760	Apr. 7, 1936	Knox, W., Jr.
2,057,956	Oct. 20, 1936	Kaselitz, O.
2,062,064	Nov. 24, 1936	Knox, W., Jr. and Cochran, R.
2,121,208	June 21, 1938	Milligan, C.
2,131,431	Sept. 27, 1938	Fiske, A.
2,138,029	Nov. 29, 1938	do
2,160,232	May 30, 1939	Schlaeger, J.
2,160,233	do	do
2,160,700	do	Knox, W., Jr.
2,160,701	do	do
2,167,432	July 25, 1939	Cox, G. and McBurney, W.
2,170,274	Aug. 22, 1939	Morgan, W.
2,181,933	Dec. 5, 1939	Block, L. and King, C.
2,182,613	do	Fiske, A.
2,222,830	Nov. 26, 1940	Moss, H. V.
2,239,543	Apr. 22, 1941	Andrews, J., *et al.*
2,263,487	Nov. 18, 1941	Cox, E. and Kean, R.
2,271,361	Jan. 27, 1942	Carpenter, F. and Enos, W.
2,272,014	Feb. 3, 1942	Knox, W., Jr.
2,272,617	Feb. 10, 1942	Cox, E., *et al.*
2,287,264	June 23, 1942	Ogburn, S., Jr.
2,288,118	June 30, 1942	Vaupel, E.
2,291,608	Aug. 4, 1942	Cobbs and Hochwalt, C.
2,291,609	do	do
2,296,495	Sept. 22, 1942	Block, E.

TABLE 27—*Concluded*

Patent No.	Date	Patentee
2,297,630	Sept. 29, 1942	Milligan, C.
2,314,090	Mar. 16, 1943	Huff, A.
2,337,491	Dec. 21, 1943	Perrin, F. and Allen, O.
2,343,456	Mar. 7, 1944	Henninger, A.
2,357,069	Aug. 29, 1944	Barackman, R.
2,359,413	Oct. 3, 1944	Freedman, L.
2,365,438	Dec. 19, 1944	Schilb, T.
2,366,857	Jan. 9, 1945	Hurka, R.
2,408,258	Sept. 24, 1946	Hetzel, E. and Taylor, G.
2,444,215	June 29, 1948	Whiteside, R. and Kolb, P.
2,445,948	July 27, 1948	Wittcoff, H.
2,447,726	Aug. 24, 1948	Allingham, W.
2,462,104	Feb. 22, 1949	Knox, W., Jr., *et al.*

TABLE 28. U. S. PATENTS ON THE MANUFACTURE AND USE OF PHOSPHATES IN WATER SOFTENERS AND DETERGENT PRODUCTS

Patent No.	Date	Patentee
284,674	Sept. 11, 1883	Rocour, G.
446,815	Feb. 17, 1891	Glaser, C.
598,182	Feb. 1, 1898	Poole, H.
744,128	Nov. 17, 1903	Strickler, E. H.
950,159	Feb. 22, 1910	Ridenour, W. E.
1,001,935	Aug. 29, 1911	Eberbach, O. A.
1,002,603	Sept. 5, 1911	Payne, E. M.
1,037,837	Sept. 3, 1912	Strickler, W. E.
1,078,655	Nov. 18, 1913	Alliger, W. T.
1,109,849	Sept. 8, 1914	Ley, Herman
1,162,024	Nov. 30, 1915	Buchner, G.
1,181,562	May 2, 1916	Barnes, J.
1,247,833	Nov. 27, 1917	Heller, Hugo
1,273,857	July 30, 1918	do
1,278,435	Sept. 10, 1918	Campbell, J. R.
1,333,393	Mar. 9, 1920	Edser, E., and Tucker, S.
1,379,735	May 21, 1921	Walker, G. T.
1,381,295	June 14, 1921	Frey, A.
1,438,588	Dec. 12, 1922	Feldenheimer, W.
1,555,474	Sept. 29, 1925	Mathias, L. D.
1,572,846	Feb. 9, 1926	Hoff, C. M.
1,613,656	Jan. 11, 1927	Hall, R. E.
1,688,112	Oct. 16, 1928	Booth, C. F., *et al.*
1,700,972	Feb. 5, 1929	do
1,711,707	May 7, 1929	Westbrook, L. R.
1,727,551	Sept. 10, 1929	Lohmann, W. H.
1,759,152	May 20, 1930	Booth, C. F., *et al.*
1,796,115	Mar. 10, 1931	Murphy, A. R., *et al.*
1,841,825	Jan. 19, 1932	Kriegsheim, H.
1,845,876	Feb. 16, 1932	Huber, H.
1,847,212	Dec. 12, 1932	Feldenheimer, W.
1,883,447	Oct. 18, 1932	Ammen, I. G.

TABLE 28—*Continued*

Patent No.	Date	Patentee
1,885,905	Nov. 1, 1932	Frost, F. L. Jr.
1,890,204	Dec. 6, 1932	Conway, B. von G., *et al.*
1,890,453	Dec. 13, 1932	Bowman, F. C.
1,891,293	Dec. 20, 1932	Girsewald, C., *et al.*
1,897,705	Feb. 14, 1933	Mandlen, H., *et al.*
1,903,041	Mar. 28, 1933	Hall, R. E., *et al.*
1,910,403	May 23, 1933	Parr, S. W. and Straub, F. G.
1,926,087	Sept. 12, 1933	Dreyfus, H., *et al.*
1,965,339	July 3, 1934	Hall, R. E.
1,972,032	Aug. 28, 1934	Reimann, A.
1,975,946	Oct. 9, 1934	Ihrig, H. K., *et al.*
2,004,809	June 11, 1935	Hall, R. E.
2,012,462	Aug. 27, 1935	Agthe, C. A., *et al.*
2,035,652	Mar. 31, 1936	Hall, R. E.
2,038,316	Apr. 21, 1936	Rosenstein, L.
2,041,473	May 19, 1936	Janota, J.
2,067,628	Jan. 12, 1937	Fiske A. H. and Bryan, C. S.
2,081,676	May 25, 1937	Neugebauer, W.
2,087,849	July 20, 1937	Wilson, J. A.
2,093,927	Sept. 21, 1937	Preston, W.
2,093,928	do	do
2,097,517	Nov. 2, 1937	Durgin, C. B.
2,121,952	June 28, 1938	Colonius, H., *et al.*
2,130,869	Sept. 20, 1938	Block, L. and Metziger, M.
2,141,189	Dec. 27, 1938	Lind, O.
2,142,180	Jan. 3, 1939	Crites, B. O.
2,142,515	do	Joos, C. E.
2,156,173	Apr. 25, 1939	Bird, P. G.
2,164,146	June 27, 1939	Reuss, W., *et al.*
2,186,095	Jan. 9, 1940	Byck, H. T., *et al.*
2,211,688	Aug. 13, 1940	Colonius, H., *et al.*
2,244,158	June 3, 1941	Hubbard, F. E. and McCullough, C.
2,257,545	Sept. 30, 1941	Curtis, F. J.
2,291,146	July 28, 1942	Buist, R. M. and Parker, M. F.
2,294,075	Aug. 25, 1942	Colgate, R. B., *et al.*
2,295,831	Sept. 15, 1942	Caryl, C. R.
2,296,767	Sept. 22, 1942	do
2,326,950	Aug. 17, 1943	Kepfer, R. J.
2,333,443	Nov. 2, 1943	Robinson, E. A.
2,333,444	do	do
2,335,466	Nov. 30, 1943	Volz, A.
2,338,987	Jan. 11, 1944	Watzel, R.
2,351,559	June 6, 1944	Treffler, A.
2,356,550	Aug. 22, 1944	Volz, A.
2,358,222	Sept. 12, 1944	Fink, G. and Richardson, H. H.
2,358,965	Sept. 26, 1944	Durgin, C. B., *et al.*
2,360,135	Oct. 10, 1944	Hull, H. H., *et al.*
2,360,730	Oct. 17, 1944	Smith, G. W.

Table 28—*Concluded*

Patent No.	Date	Patentee
2,365,190	Dec. 19, 1944	Hatch, G. B.
2,365,215	do	Rhodes, J. C.
2,370,472	Feb. 27, 1945	King, C.
2,370,473	do	do
2,374,100	Apr. 17, 1945	Jackson, H. A.
2,376,096	May 15, 1945	Snell, F. D.
2,380,259	July 10, 1945	Pierce, F. E.
2,381,124	Aug. 7, 1945	Hart, J. F.
2,381,960	Aug. 14, 1945	Johnson, A. D.
2,382,163	do	MacMahon, J. D.
2,382,164	do	do
2,383,502	Aug. 28, 1945	Quimby, O. T.
2,383,610	do	Morgan, J. D., *et al.*
2,385,928	Oct. 2, 1945	Meites, L.
2,385,929	do	do
2,387,572	Oct. 23, 1945	Flett, L. H.
2,394,320	Feb. 5, 1946	McGhie, R. P.
2,395,126	Feb. 19, 1946	King, C. S.
2,396,278	Mar. 12, 1946	Lind, Otto
2,404,289	July 16, 1946	Hicks, W. B., *et al.*
2,405,276	Aug. 6, 1946	Taylor, A. G.
2,409,718	Oct. 22, 1946	Snell, F. D., *et al.*
2,411,090	Nov. 12, 1946	Garverich, E. S., *et al.*
2,412,819	Dec. 17, 1946	MacMahon, J. D.
2,414,969	Jan. 28, 1947	Moose, J. E.
2,419,147	Apr. 15, 1947	King, C.
2,419,148	do	do
2,421,703	June 3, 1947	Kamlet, J.
2,426,394	Aug. 26, 1947	Hall, R. E. and Munter, C. I.
2,427,642	Sept. 16, 1947	Aitchison, A. G.
2,431,946	Dec. 2, 1947	Lurie, D.
2,434,674	Jan. 20, 1948	Pincus, A. G.
2,435,453	Feb. 3, 1948	MacMahon, J. D.
2,436,670	Feb. 24, 1948	Russell, C. H.
2,444,836	July 6, 1948	MacMahon, J. D.
2,455,050	Nov. 30, 1948	Eisenberger, S., *et al.*
2,455,648	Dec. 7, 1948	Bennett, W. R.
2,471,645	May 31, 1949	Morris, M. M., *et al.*
2,473,822	June 21, 1949	Robinson, E. A.
2,480,730	Aug. 30, 1949	Hafford, B. C., *et al.*
2,486,921	Nov. 1, 1949	Byerly, D. R.
2,494,827 \ 2,494,828 /	Jan. 17, 1950	Munter, C. J.
2,503,381	Apr. 11, 1950	Eichwald, E.
2,509,440	May 30, 1950	Little, L. L.
2,510,510	June 6, 1950	Mendenhall, E. E.
2,519,747	Aug. 27, 1950	Dubois, A. S.
2,522,446 \ 2,522,477 /	Sept. 12, 1950	Harris, J. C.
2,531,166	Nov. 21, 1950	Shaw, C. M.

TABLE 28-A. U. S. PATENTS ON ESTERS OF PHOSPHORIC ACID AND
THEIR APPLICATIONS

Patent No.	Date	Patentee
700,000	May 27, 1902	Zuhl, E.
1,425,393	Aug. 8, 1922	Laska, A. L. and Prillwitz, H. H. C.
1,766,720	June 24, 1930	Nicolai, F.
1,785,951	Dec. 23, 1930	Gibson, W., *et al.*
1,799,349	Apr. 7, 1931	Bannister, W. J.
1,837,176	Dec. 15, 1931	Horst, William P.
1,852,231	Apr. 5, 1932	Bryner, F.
1,856,862	May 3, 1932	do
1,884,433	Oct. 25, 1932	Webb, W. R. and Clarke, H. P.
1,931,056	Oct. 17, 1933	Clemmensen, E.
1,932,130	Oct. 24, 1933	Blagden, J. W. and Huggett, W. E.
1,944,530	Jan. 23, 1934	Schonburg, C.
1,958,210	May 8, 1934	Scott, W.
1,959,228	May 15, 1934	Blagden, J. W. and Huggett, W. E.
1,977,973	Oct. 23, 1934	Rohm, O.
1,982,903	Dec. 4, 1934	Clemmensen, E.
2,005,619	June 18, 1934	DeWitt, G.
2,008,478	July 16, 1935	Vanderbilt, B. M. and Gottlieb, M. B.
2,026,785	Jan. 7, 1936	Harris, B. R.
2,044,773	June 23, 1936	Conn, W. T.
2,046,031	June 30, 1936	Mugdan, M. and Sixt, J.
2,052,029	Aug. 26, 1936	Harris, B. R.
2,053,653	Sept. 8, 1936	Butz, K.
2,058,342	Oct. 20, 1936	Moran, R. C., *et al.*
2,058,344	do	Moran, R. C., *et al.*
2,059,084	Oct. 27, 1936	Buchheim, K.
2,062,312	Dec. 1, 1936	Ipatieff, V. and Shuman, R. L.
2,078,421	Apr. 27, 1937	Shuman, R. L.
2,071,323	Feb. 23, 1937	Bass, S. L.
2,119,523	June 7, 1938	Butz, C.
2,112,514	July 5, 1938	Crocker, E. C. and Billings, H. J.
2,133,310	Oct. 18, 1938	Shuman, R. L.
2,149,937	Mar. 7, 1939	Copley, M. J.
2,161,455	June 6, 1939	Clifford, A. M.
2,175,509	Oct. 10, 1939	Rogers, T. H., *et al.*
2,175,877	do	Clark, F. M.
2,182,309	Dec. 5, 1939	Britton, E. C. and Moyle, C. L.
2,182,817	Dec. 12, 1939	Moyle, C. L.
2,184,697	Dec. 26, 1939	Havermann, H. and Smeykal, K.
2,188,322	Jan. 30, 1940	Tattersall, H. J.
2,190,769	Feb. 20, 1940	Butz, K.
2,200,712	May 14, 1940	Carswell, T. C.
2,200,485	do	Brodersen, K. and Quaedvlieg, M.

TABLE 28-A—*Continued*

Patent No.	Date	Patentee
2,207,233	July 9, 1940	Streng, F.
2,213,513	Sept. 3, 1940	Bancroft, W. D., *et al.*
2,213,514	do	do
2,213,515	do	do
2,213,619	do	do
2,213,620	do	do
2,218,582	Oct. 22, 1940	Lindner, K.
2,219,050	Oct. 22, 1940	Mikeska, L. A.
2,220,113	Nov. 5, 1940	Moyle, C. L.
2,223,329	Nov. 26, 1940	do
2,223,548	Dec. 3, 1940	Caplan, S.
2,224,695	Dec. 10, 1940	Prutton, C. F.
2,228,658	Jan. 14, 1941	Farrington, B. B. and Clayton, J. O.
2,228,659	do	do
2,228,671	Jan. 14, 1941	Neeley, G.L. and Gardiner, E.W.
2,231,946	Feb. 18, 1941	Rechel, E.R. and Stevenson, T.
2,237,632	Apr. 8, 1941	Ries, H. E., Jr.
2,237,866	do	do
2,241,243	May 6, 1941	Conary, R.E. and Ashburn, H.V.
2,241,244	do	do
2,244,705	June 10, 1941	Hutchinson, J. F. and Schilling, A. A.
2,250,662	July 29, 1941	Walter, J. M.
2,250,663	do	do
2,262,634	Nov. 11, 1941	Cobbs, W. W.
2,268,387	Dec. 30, 1941	Flenner, A. L. and Fauffert, F. H.
2,271,044	Jan. 27, 1942	Schilling, A. A.
2,273,781	Feb. 17, 1942	Hochwalt, C. A.
2,274,447	Feb. 24, 1942	Hodgins, T. S. and Hovey, A. G.
2,275,041	Mar. 3, 1942	Britton, E. C. and Moyle, C. L.
2,278,747	Apr. 7, 1942	Swezey, F. H., *et al.*
2,286,308	June 16, 1942	Rosser, C. M.
2,289,795	July 14, 1942	McNab, J. G.
2,329,707	Sept. 20, 1943	Farrington, F. L., *et al.*
2,345,690	Apr. 4, 1944	Solmssen, U. V.
2,373,807	Apr. 17, 1945	Beeg, H. and Schmidt, R.
2,382,622	Aug. 14, 1945	Toy, A. D. F.
2,382,775	do	Cook, E. W. and Thomas, W. D., Jr.
2,386,207	Oct. 9, 1945	Reiff, O. M. and Andress, H. J., Jr.
2,387,537	Oct. 23, 1945	Smith, H. G., *et al.*
2,394,829	Feb. 12, 1946	Whitehill, L. N. and Barker, R. S.
2,410,118	Oct. 29, 1946	Woodstock, W. H. and Pelletier, P. E.
2,430,569	Nov. 11, 1947	Hull, D. C. and Agett, A. M.
2,441,295	May 11, 1948	Smith, H. G. and Cantrell, T. L.
2,442,582	June 1, 1948	Bishop, J. W.

TABLE 28-A—*Concluded*

Patent No.	Date	Patentee
2,443,473	June 15, 1948	Milas, A.
2,452,319	Oct. 27, 1948	Patterson, J. A., and Kluge, H. B.
2,460,043	Jan. 25, 1949	Teeters, W. O.
2,466,393	Apr. 5, 1949	McNally, J. G.
2,473,612	June 21, 1949	Shuman, R. L.
2,475,143	July 5, 1949	Kemp, L. C.
2,478,441	Aug. 9, 1949	Wiley, R. H.
2,482,063	Sept. 13, 1949	Hechenbleikner, I.
2,490,573	Dec. 6, 1949	Ratcliff, F., *et al.*
2,490,748	do	Dickey, J. B. and McNally, J. G.
2,493,597	Jan. 3, 1950	Rothrock, D. A., Jr., *et al.*
2,494,310	Jan. 10, 1950	Plueddemann, E. P.
2,495,220	Jan. 24, 1950	Bell, A.
2,499,503	Mar. 7, 1950	Huff, C. E., *et al.*
2,500,022	do	Brown, J. H.
2,502,401	Mar. 28, 1950	Harris, L. W., *et al.*
2,503,204	Apr. 4, 1950	Kosolapoff, G. M.
2,504,165	Apr. 18, 1950	Toy, A. D. F.
2,508,389	Apr. 23, 1950	Hull, D. C., *et al.*
2,510,033	May. 30, 1950	Kyrides, L. P.
2,512,282	June 20, 1950	Plueddemann, E. P.
2,514,150	July 4, 1950	Bell, A.
2,514,621	July 11, 1950	do
2,518,692	Aug. 15, 1950	Hull, D. C., *et al.*
2,523,243	Sept. 19, 1950	Willis, N. E.
2,523,252	do	Smith, F. D., *et al.*
2,523,613	Sept. 26, 1950	Dvornikoff, M. N., *et al.*
2,531,354	Nov. 21, 1950	Dvornikoff, M. N.

TABLE 29. U. S. PATENTS ON PHOSPHATE COATINGS FOR METAL SURFACES

Patent No.	Date	Patentee
870,937	Nov. 12, 1907	T. W. Coslett
1,007,069	Oct. 31, 1911	do
1,069,903	Aug. 12, 1913	F. R. Granville
1,167,966	Jan. 11, 1916	W. H. Allen
1,206,075	Nov. 28, 1916	do
1,211,218	Jan. 2, 1917	C. W. Parker
1,215,463	Feb. 13, 1917	W. H. Allen
1,219,526	Mar. 20, 1917	do
1,221,046	Apr. 3, 1917	J. H. Gravell
1,221,441	do	do
1,221,442	do	do
1,240,395	Sept. 18, 1917	D. C. Westerfield
1,247,660	Nov. 27, 1917	R. L. Gooding
1,248,053	do	W. H. Allen
1,254,263	Jan. 22, 1918	W. I. Oeschger
1,254,264	do	do
1,260,740	Mar. 26, 1918	W. H. Allen
1,263,395	Apr. 23, 1918	W. R. Emig

TABLE 29—*Continued*

Patent No.	Date	Patentee
1,271,002	July 2, 1918	W. H. Allen
1,273,358	July 23, 1918	J. H. Gravell
1,287,605	Dec. 17, 1918	W. H. Allen
1,290,476	Jan. 7, 1919	do
1,291,352	Jan. 14, 1919	do
1,303,627	May 13, 1919	H. C. Baines
1,311,319	July 29, 1919	R. D. Colquhoun
1,317,351	Sept. 30, 1919	L. S. Chadwick and M. Resek
1,320,734	Nov. 4, 1919	do
1,329,573	Feb. 3, 1920	W. H. Allen
1,341,100	May 25, 1920	do
1,344,372	June 22, 1920	H. C. Baines
1,381,112	June 14, 1921	Emig, W. R.
1,388,325	Aug. 23, 1921	L. S. Chadwick
1,428,084	Sept. 5, 1922	J. H. Gravell
1,428,086	do	do
1,428,087	do	do
1,485,025	Feb. 26, 1924	M. Green
1,493,012	May 6, 1924	C. E. Abrahams
1,525,904	Feb. 10, 1925	W. H. Allen
1,549,410	Aug. 11, 1925	J. H. Gravell
1,561,053	Nov. 10, 1925	B. K. Brown and G. Schmidt
1,572,354	Feb. 9, 1926	J. H. Gravell
1,592,102	July 13, 1926	do
1,610,362	Dec. 14, 1926	T. W. Coslett
1,639,694	Aug. 23, 1927	M. Green and H. H. Willard
1,651,694	Dec. 6, 1927	M. Green, E. M. Jones and H. H. Willard
1,654,716	Jan. 3, 1928	W. H. Allen
(Reissue) 17,484	Nov. 12, 1929	
1,658,222	Feb. 7, 1928	Burns, *et al.*
1,660,661	Feb. 28, 1928	M. Green and H. H. Willard
1,663,446	Mar. 20, 1928	C. F. Dinley
1,677,667	May 28, 1929	Zimmerman
(Reissue-17,309)		
1,709,894	Apr. 23, 1929	E. C. Burdick
1,713,653	May 21, 1929	J. H. Cravell
1,719,463	July 2, 1929	W. H. Cole
1,735,842	Nov. 19, 1929	W. H. Allen
1,750,270	Mar. 11, 1930	E. M. Jones
1,752,746	Apr. 1, 1930	J. D. Klinger and C. Boyle
1,755,391	Apr. 22, 1930	M. Green and V. M. Darsey
1,761,186	June 3, 1930	M. C. Baker and W. A. Dingman
1,765,341	June 17, 1930	R. E. Lowe
1,769,057	July 1, 1930	M. Green and E. M. Jones
1,781,507	Nov. 11, 1930	J. H. Gravell
1,790,960	Feb. 3, 1931	E. K. Wallace
1,791,715	Feb. 10, 1931	V. M. Darsey
1,791,082	Feb. 3, 1931	Giuseppe Bianeo

<div align="center">TABLE 29—<i>Continued</i></div>

Patent No.	Date	Patentee
1,826,866	Oct. 13, 1931	W. H. Cole
1,832,979	Nov. 24, 1931	H. S. George
1,837,430	Dec. 22, 1931	J. H. Gravell
1,839,523	Jan. 5, 1932	W. H. Allen
1,842,085	Jan. 19, 1932	M. Green and E. M. Jones
1,856,261	May 3, 1932	W. M. Phillips and G. M. Cole
1,866,879	July 12, 1932	V. M. Darsey
1,869,121	July 26, 1932	J. S. Thompson and R. R. Tanner
1,872,507	Aug. 16, 1932	S. G. Saunders and C. C. Williams
1,873,363	Aug. 23, 1932	R. R. Tanner
1,887,967	Nov. 15, 1932	R. R. Tanner and V. M. Darsey
1,888,189	do	do
1,911,726	May 30, 1933	R. R. Tanner and H. J. Lodeesen
1,926,265	Sept. 12, 1933	V. M. Darsey
1,926,266	do	do
1,949,090	Feb. 27, 1934	R. R. Tanner and H. J. Lodeesen
1,992,045	Feb. 19, 1935	W. K. Schweitzer
2,001,754	May 21, 1935	J. S. Thompson and V. M. Darsey
2,030,601	Feb. 11, 1936	G. A. McDonald
2,041,545	May 19, 1936	C. E. Heussner
2,045,499	June 23, 1936	R. R. Tanner and H. J. Lodeesen
2,059,783	Nov. 3, 1936	G. J. Farnworth
2,067,007	Jan. 5, 1937	V. M. Darsey
2,067,214	Jan. 12, 1937	R. R. Tanner and J. S. Thompson
2,067,215	do	do
2,067,216	do	J. S. Thompson and H. J. Lodeesen
2,070,487	Feb. 9, 1937	G. Lutz
2,082,950	June 8, 1937	M. Green
2,089,648	Aug. 10, 1937	R. H. Gordon
2,097,211	Oct. 26, 1937	H. T. Davies
2,120,212	June 7, 1938	L. P. Curtin
2,121,520	June 21, 1938	do
2,121,574	do	G. C. Romig
2,127,207	Aug. 16, 1938	L. P. Curtin
2,132,000	Oct. 4, 1938	do
2,163,583	June 27, 1939	R. W. Buzzard
2,163,984	do	Pelkovie, V. A.
2,164,042	do	G. C. Romig
2,186,177	Jan. 9, 1940	do
2,191,435	Feb. 27, 1940	J. H. Ballard and W. H. Spencer
2,194,491	Mar. 26, 1940	P. C. Bird, *et al.*
2,208,524	July 16, 1940	V. M. Darsey and H. J. McVey
2,213,263	Sept. 3, 1940	J. S. Thompson and H. K. Ward
2,228,836	Jan. 14, 1941	J. MacQuaid
2,233,422	Mar. 4, 1941	H. J. Lodeesen
2,234,206	Mar. 11, 1941	J. S. Thompson
2,236,549	Apr. 1, 1941	V. M. Darsey, *et al.*
2,272,216	Feb. 10, 1942	H. J. Lodeesen
2,293,716	Aug. 25, 1942	V. M. Darsey

TABLE 29—*Continued*

Patent No.	Date	Patentee
2,295,063	Sept. 8, 1942	J. N. Tuttle
2,295,545	Sept. 15, 1942	W. J. Clifford and H. H. Adams
2,296,070	do	J. S. Thompson and E. W. Goodspeed
2,296,844	Sept. 29, 1942	C. W. Glasson
2,298,280	Oct. 13, 1942	W. J. Clifford and H. H. Adams
2,298,312	do	G. C. Romig
2,301,209	Nov. 10, 1942	R. C. Gibson
2,302,510	Nov. 17, 1942	R. R. Tanner and H. J. Lodeesen
2,303,242	Nov. 24, 1942	R. R. Tanner and R. V. Harris
2,306,143	Dec. 22, 1942	A. E. Stevenson
2,310,239	Feb. 9, 1943	G. W. Jernstedt
2,311,240	Feb. 16, 1943	C. A. Marien, *et al.*
2,312,855	Mar. 2, 1943	J. S. Thompson
2,314,565	Mar. 23, 1943	do
2,314,887	Mar. 30, 1943	H. J. Lodeesen and H. K. Ward
2,316,810	Apr. 20, 1943	G. C. Romig
2,316,811	do	do
2,318,606	May 11, 1943	M. T. Goehel, *et al.*
2,318,642	do	J. S. Thompson
2,318,656	do	do
2,322,349	June 22, 1943	O. W. Jernstedt
2,326,309	Aug. 10, 1943	G. C. Romig
2,327,127	Aug. 17, 1943	F. E. Rath
2,329,065	Sept. 7, 1943	J. C. Lum and G. Jernstedt
2,331,196	Oct. 5, 1943	do
2,335,868	Dec. 7, 1943	H. J. Lodeesen
2,336,020	do	H. J. Krase
2,336,071	do	W. J. Clifford and H. H. Adams
2,336,072	do	do
2,336,448	do	Edwin, Cox
2,342,738	Feb. 29, 1944	Jernstedt, G. W.
2,346,302	Apr. 11, 1944	H. E. Hays, G. R. Hoover and A. E. Taylor
2,348,698	May 9, 1944	J. S. Thompson
2,351,605	June 20, 1944	R. C. Gibson
2,373,433	Apr. 10, 1945	R. R. Tanner
2,375,468	May 8, 1945	W. J. Clifford and H. H. Adams
2,394,065	Feb. 5, 1946	G. W. Jernstedt
2,398,212	Apr. 9, 1946	C. B. Durgin
2,403,426	July 2, 1946	G. C. Romig and A. Douty
2,412,543	Dec. 10, 1946	R. R. Tanner
2,418,608	Apr. 8, 1947	J. S. Thompson and R. R. Tanner
2,438,013	Mar. 16, 1948	R. R. Tanner
2,438,877	Mar. 30, 1948	F. P. Spruance, Jr.
2,449,495	Sept. 14, 1948	Lum, J. C.
2,452,321	Oct. 26, 1948	Kluge, H. D. and Patterson, J. A.
2,462,196	Feb. 22, 1949	Jernstedt, G. W.
2,463,496	Mar. 1, 1949	Russell, W. S.

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Table 29—*Concluded*

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Patent No.	Date	Patentee
2,472,099	June 7, 1949	Engle, L. S. and Fikar, W.
2,472,864	June 14, 1949	Spruance, F. P., Jr., *et al.*
2,473,614	June 21, 1949	Snyder, E.
2,475,944	July 12, 1949	Clark, C. W. and Scholen, J. H.
2,475,945	do	Clark, C. W. and Collins, T. C.
2,475,946	do	do
2,477,841	Aug. 2, 1949	Ward, H. K.
2,478,954	Aug. 16, 1949	Tuttle, B. S. and Navoy, T.
2,479,564	do	Gilbert, L. O.
2,486,664	Nov. 1, 1949	Marling, P. E., *et al.*
2,490,062	Dec. 6, 1949	Jernstedt, G. W.
2,494,908	Jan. 17, 1950	Spruance, F. P., *et al.*
2,494,910	do	Spruance, F. P., Jr.
2,499,261	Feb. 28, 1950	Rosenbloom, H. I.
2,500,673	Mar. 14, 1950	Gibson, R. C., *et al.*
2,502,441	Apr. 4, 1950	Dodd, S. R., *et al.*
2,512,590	June 20, 1950	Swain, R. C.
2,516,139	July 25, 1950	Mazia, J.
2,524,357	Oct. 3, 1950	Robey, P.
2,527,828	Oct. 31, 1950	Kruszynski, E. A., *et al.*
2,528,787	Nov. 7, 1950	Roland, C. T.
2,529,206	do	Winslow, A. F., *et al.*

TABLE 30. U. S. PATENTS CONCERNED WITH BONE CHAR TECHNOLOGY[1]

Patent No.	Date	Patentee	Title
12,602	Mar. 27, 1855	McNeill	Charcoal-furnace
13,740	Oct. 30, 1855	Bertrand, C. E.	Improvement in sugar-filters
22,734	Jan. 25, 1859	Kattenhorn, H.	Improvement in revivification of bone-black
26,457	Dec. 13, 1859	Bellows, W.	Improvement in revivifying bone-black
27,462	Mar. 13, 1860	Mitchell, W.	Improvement in apparatus for revivifying bone-black
29,128	July 10, 1860	Kinzler, C.	Apparatus for washing bone-black
32,679	July 2, 1861	Brock, C. N.	Improvement in apparatus for revivifying bone-black
35,160	May 6, 1862	Leplay, A. H., Cuisinier, J. F. J.	Improvement in revivifying animal charcoal for refining sugar
35,212	May 13, 1862	Brison, C.	Improvement in furnaces for retorts, stills, etc.
36,230	Aug. 19, 1862	Moller, W.	Improved oven for reburning bone-black
39,637	Aug. 25, 1863	Finken, G.	Improved apparatus for revivifying bone-black
39,638	do	Forrest, J.	Improvement in revivifying bone-black
40,371	Oct. 20, 1863	Thulemeyer, G.	Improvement in furnaces for reburning bone-black
47,308	Apr. 18, 1865	Jasper, G. A.	Improvement in cleansing and revivifying charcoal
53,534	Mar. 27, 1866	do	Improvement in cleansing animal charcoal
54,771	May 15, 1866	Quick, T. H.	Improvement in purifying bone-black
60,492	Dec. 18, 1866	Eastwick, E. P.	Improvement in bone-black kilns
61,851	Feb. 5, 1867	Moller, W.	Improvement in cooling animal coal
62,537	Mar. 5, 1867	Ficken, R., Williams, F. L.	Improved machine for cleaning and purifying bone-black
62,927	Mar. 19, 1867	Bradford, W. R.	Improved cover for kilns of sugar refiners
65,389	June 4, 1867	Jasper, G. A.	Improvement in retorts for revivifying bone charcoal
65,457	do	Weber, A.	Improvement in kilns for reburning and purifying bone-black

[1] List prepared by Victor R. Deitz, National Bureau of Standards.

TABLE 30—*Continued*

Patent No.	Date	Patentee	Title
65,597	June 11, 1867	Pierce, C. W.	Improvement in the construction of pots for charring or burning bones
68,915	Sept. 17, 1867	Turner, D. H.	Improvement in cooling and purifying animal charcoal
71,536	Nov. 26, 1867	Quick, T. H.	Improvement in purifying bone-black
77,935	May 12, 1868	Turner, D. H.	Improved apparatus for cooling and purifying bone-black
87,653	Apr. 6, 1869	Endemann, H.	Improved artificial bone-black
88,700	do	Eastwick, E. P.	Improved bone-black kiln
88,701	do	do	Improvement in kilns for burning bone-black
88,702	do	do	Improved kiln for bone-black
89,492	Apr. 27, 1869	McCann, J.	Improved retort for preparing charcoal for rectifying spirits, etc.
90,097	May 18, 1869	Hanford, M.	Improved apparatus for purifying, screening, and cooling reburnt bone-black
92,751	July 20, 1869	Rogers, J., Reid, L.	Improvement in treating and revivifying bone-black
93,208	Aug. 3, 1869	Langen, E.	Improved apparatus for emptying the cooling-tubes of bone-black furnaces.
93,668	Aug. 17, 1869	Brasill, D., Mullane, D. A.	Improved bone-black equalizer
96,899	Nov. 16, 1869	Donner, J. O.	Improved kiln for revivifying bone-black
101,019	Mar. 22, 1870	Jasper, G. A.	Improved apparatus for cooling and saving charcoal
105,747	July 26, 1870	Weber, A.	Improvement in furnaces for reburning bone-black and reducing ores
113,279	Apr. 4, 1871	Eissfeldt, H., Thumb, C.	Improvement in purifying animal charcoal
113,754	Apr. 18, 1871	Farley, P.	Improvement in drying bone-black
114,780	May 16, 1871	Eastwick, E. P.	Improvement in kilns for reburning bone-black
116,361	June 27, 1871	Senff, C. H.	Improvement in apparatus for cooling bone-black
119,005	Sept. 19, 1871	Beach, C. Y.	Improvement in the manufacture of bone-black

TABLE 30—*Continued*

Patent No.	Date	Patentee	Title
122,526	Jan. 9, 1872	Kelsey, W. H.	Improvement in artificial bone-black for filtering
134,686	Jan. 7, 1873	Lonsky, A.	Improvement in apparatus and processes for revivifying bone-black
150,821	May 12, 1874	Buchanan, J., Vickess,	Improvement in treating animal charcoal or bone-black
153,741	Aug. 4, 1874	Billitz, S.	Improvement in the manufacture of bone-black
155,919	Oct. 13, 1874	Blau, S.	Improvement in the manufacture of bone-black
158,166	Dec. 29, 1874	Colwell, L.	Improvement in drying apparatus for animal char
161,253	Mar. 23, 1875	Matthiessen, F. O.	Improvement in retorts for burning or revivifying charcoal
165,344	July 6, 1875	Lugo, O.	Improvement in processes of manufacturing animal charcoal
165,992	July 27, 1875	Gandolfo, J.	Improvement in apparatus for burning and revivifying bone-black, etc.
167,235	Aug. 31, 1875	Gandolfo, J.	Improvement in bone-black revivifiers
173,989	Feb. 22, 1876	Ockershausen, G. P.	Improvement in furnaces for the manufacture of bone-black
178,286	June 6, 1876	Gandolfo, J.	Improvement in apparatus for burning and revivifying bone-black
178,315	June 6, 1876	Lugo, O.	Improvement in preparing bone-black
179,579	July 4, 1876	do	Improvement in treating and revivifying bone-black or animal charcoal
186,327	Jan. 16, 1877	Doscher, C.	Improvement in apparatus for cooling bone-black
188,006	Mar. 6, 1877	Elmenhorst, W. R.	Improvement in bone-black kilns
188,029	do	Quimby, E. E.	Improvement in bone-black retorts
190,676	May 15, 1877	Gandolfo, J.	Improvement in bone-black revivifiers
194,256	Aug. 14, 1877	McKeever, E. A.	Improvement in recovery of spirits from spent charcoal of rectifying-filters

TABLE 30—*Continued*

Patent No.	Date	Patentee	Title
199,118	Jan. 8, 1878	Stillman, O. B., Webster, J. H.	Improvement in measuring and discharging apparatus for cooling-tubes of char-furnaces
221,725	Nov. 18, 1879	Davis, G. D.	Improvement in retorts and furnaces for calcining bones
235,942	Dec. 28, 1880	Elmenhorst, W. R.	Kiln for drying and revivifying bone-black
236,458	Jan. 11, 1881	Richards, E. K.	Discharging apparatus for bone-black furnaces
239,962	Apr. 12, 1881	Jennings, R. S.	Apparatus for recarbonizing charcoal in filters
247,388	Sept. 20, 1881	Meyer, G. F.	Method of filtration
249,004	Nov. 1, 1881	Chesebrough, R. A.	The art of and apparatus for making and revivifying bone-black
254,474	Mar. 7, 1882	Goubert, A. A.	Automatic discharging apparatus for bone-black kilns, etc.
257,114	Apr. 25, 1882	Webster, J. H., Stillman, O. B.	Measuring and discharging apparatus for cooling-tubes of char-furnaces
260,486	July 4, 1882	Lillie, M. S.	Process of treating new bone-black and of revivifying old bone-black
263,710	Sept. 5, 1882	do	Process of washing bone-black in sugar-refineries and apparatus for carrying on the same
265,723	Oct. 10, 1882	Weber, A.	Furnace for burning and revivifying bone-black
265,876	do	Schafer, A.	Bone and wood burner
268,981	Dec. 12, 1882	Barr, R. J.	Discharge apparatus for coolers of bone-black kilns
274,901	Apr. 3, 1883	Breer, H.	Apparatus for treating animal matter for fertilizers
278,356	May 29, 1883	Niese, H. E., Dinkel, G.	Apparatus for cooling or drying granular materials
279,335	June 12, 1883	Clark, R. C.	Process of renewing bone-black
286,056	Oct. 2, 1883	Newhall, G. M.	Machine for drying sugar and other substances
287,570	Oct. 30, 1883	Osmer, F.	Apparatus for taking off ammonia from bone-black retorts
293,430	Feb. 12, 1884	Eastwick, E. P.	Apparatus for revivifying bone-black

TABLE 30—*Continued*

Patent No.	Date	Patentee	Title
297,948	Apr. 29, 1884	Osmer, F.	Apparatus for taking off ammonia from bone-black retorts
303,378	Aug. 12, 1884	Matthiessen, F. O.	Bone-black kiln
303,379	do	do	Bone-black kiln
308,476	Nov. 25, 1884	Eastwick, E. P.	Bone-black kiln
314,866	Mar. 31, 1885	Murdoch, G.	Bone-black oven
316,610	Apr. 28, 1885	Eastwick, E. P.	Top plate for bone-black kilns
320,110	June 16, 1885	Zwillinger, A.	Apparatus for carbonizing bones, etc.
329,184	Oct. 27, 1885	Matthiessen, F. O.	Continuous filter for filtering sugar-liquor
329,185	do	do	Bone-black filter for filtering sugar-liquors
329,210	do	Quimby, E. E.	Apparatus for decolorizing sugar-liquor by upward filtration through bone-black
329,305	do	Gaunt, T.	Bone-black discharger for continuous filters
329,306	do	do	Bone-black filter for filtering saccharine liquids
329,324	do	Lillie, M. S.	Bone-black drier
329,329	do	Matthiessen, F. O.	Bone-black filter
329,330	do	do	Apparatus for decolorizing saccharine and other liquids by filtration through bone-black
329,332	do	do	Apparatus for decolorizing sugar-liquor by upward filtration through bone-black
335,137	Feb. 2, 1886	Lillie, S. M.	Process of and apparatus for drying bone-black
335,586	Feb. 9, 1886	Howes, R. C.	Bone-black discharger for continuous filters
335,602	do	Matthiessen, F. O.	Bone-black discharger for continuous filters
335,603	do	do	Bone-black discharger for continuous filters
335,622	do	Quimby, E. E.	Continuous filter for purifying sugar-liquors by bone-black
335,763	do	Matthiessen, F. O.	Apparatus for decolorizing sugar-liquor by filtration through bone-black
337,411	Mar. 9, 1886	Lillie, S. M.	Process of utilizing the waste heat from bone-black-revivifying kilns

TABLE 30—*Continued*

Patent No.	Date	Patentee	Title
340,005	Apr. 13, 1886	Quimby, E. E.	Draining device for upwardly-acting bone-black filters
341,497	May 11, 1886	Newhall, G. M., Colwell, A. W.	Bone-black drier
343,666	June 15, 1886	Lillie, S. M.	Apparatus for drying bone-black in sugar-refineries
345,324	July 13, 1886	Schmandt, C. H. C.	Bone-black kiln
345,968	July 20, 1886	Harrison, A. C.	Retort for calcining bone-black
350,170	Oct. 5, 1886	Stillman, J. F.	Bone-black revivifier
351,929	Nov. 2, 1886	Lillie, S. M.	Bone-black drier
360,581	Apr. 5, 1887	Gaukroger, A.	Screen-bottom for char charcoal washing and filtering tanks
391,335	Oct. 16, 1888	Porter, C. L.	Apparatus for restoring the spent properties of charcoal
407,912	July 30, 1889	Weber, A.	Furnace for burning bone black
407,976	do	do	Kiln for burning bone-black
409,873	Aug. 27, 1889	Scherffius, J.	Charcoal apparatus
412,781	Oct. 15, 1889	McNab, J.	Furnace for calcining bone-black
414,552	Nov. 5, 1889	Langen, E.	Furnace for roasting or otherwise treating granular or pulverulent materials
414,608	do	Urbain, E.	Ground-bone furnace
429,682	June 10, 1890	Guinon, R. V. F. de	Apparatus for treating charcoal
447,313	Mar. 3, 1891	Grimm, J. H., Pennypacker, W. G.	Apparatus for reburning animal charcoal
450,209	Apr. 14, 1891	Whiddit, W. W.	Recarbonizer for filters
509,460	Nov. 28, 1893	Weinrich, M.	Process of revivifying bone-black
523,248	July 17, 1894	Trory, James T.	Bone-black kiln
526,180	Sept. 18, 1894	Dubbs, Jesse A.	Treatment of animal charcoal
529,469	Nov. 20, 1894	Spreckels, Claus	Apparatus for heating water in sugar-refineries
530,632	Dec. 11, 1894	Weinrich, Moriz	Apparatus for decarbonizing and revivifying bone-black
533,106	Jan. 29, 1895	do	Process of revivifying bone-black
538,028	Apr. 23, 1895	Scribner, Edwin A.	Apparatus for treatment of bone-black
556,603	Mar. 17, 1896	Wheeler	Bone-black kiln
557,498	Mar. 31, 1896	Eba, Bernhardt	Kiln for revivifying bone-black

TABLE 30—*Continued*

Patent No.	Date	Patentee	Title
584,071	June 8, 1897	Booraem, John V. V.	Apparatus for revivifying char
585,658	July 6, 1897	Donner, John O.	Apparatus for decarbonizing bone-black
586,278	July 13, 1897	Weinrich, Moriz	Revivifying bone-black
587,057	July 27, 1897	Jarves, Deming	Retort
592,547	Oct. 26, 1897	Krause, Arthur E.	Apparatus for revivifying bone-black
612,319	Oct. 11, 1898	Eba, Bernhardt	Bone-black kiln
617,080	Jan. 3, 1899	Catlett, Charles	Revivifying bone-black
624,510	May 9, 1899	Lister, Edwin	Bone-black kiln
638,177	Nov. 28, 1899	Eba, Bernhardt	Bone-black kiln
644,507	Feb. 27, 1900	do	Bone-black retort
708,898	Sept. 9, 1902	Mohr, W. T.	Bone-black kiln
742,723	Oct. 27, 1903	Newhall, G. M.	Char-Drier
769,421	Sept. 6, 1904	Weinrich, Moriz	Apparatus for drying bone-black
796,303	Aug. 1, 1905	Eba, Bernhardt	Bone-black kiln
796,304	do	do	Bone-black kiln
831,805	Sept. 25, 1906	Siebel, John E.	Process of treating bone-black
851,409	Apr. 23, 1907	Duisdieker, Charles H.	Retort
871,705	Nov. 19, 1907	Kent, Robert S.	Apparatus for drying charcoal
912,644	Feb. 16, 1909	Bennett, Robert	Retort
914,052	Mar. 2, 1909	Kent, R. S.	Apparatus for drying finely-divided material
940,520	Nov. 16, 1909	Eba, B.	Bone-black kiln
947,503	Jan. 25, 1910	Utley, J. H.	Process of purifying animal charcoal and the product thereof
961,180	June 14, 1910	do	Bone-black filter for clarifying gelatin liquors and the like
972,002	Oct. 4, 1910	Kent, R. S.	Kiln for revivifying char
972,023	do	Ritchay, V. O., Besselman, F. W.	Bone-burner
978,625	Dec. 13, 1910	Nichols, O. P.	Bone-black furnace
984,931	Feb. 21, 1911	Kent, R. S.	Apparatus for drying charcoal
1,004,176	Sept. 26, 1911	do	Kiln for revivifying char
1,052,113	Feb. 4, 1913	Wiese, H.	Process for refining sugar
1,058,369	Apr. 8, 1913	Kent, R. S.	Kiln for drying char
1,084,772	Jan. 20, 1914	Weinrich, M.	Process of defecating raw cane-sugar or cane-sugar syrup
1,121,429	Dec. 15, 1914	do	Apparatus for drying bone-black
1,133,049	Mar. 23, 1915	McKee, R. H.	Purification of liquids

TABLE 30—*Continued*

Patent No.	Date	Patentee	Title
1,135,216	Apr. 13, 1915	Spanutius, F. W.	Process for making a decolorizer
1,146,265	July 13, 1915	Kent, R. S.	Apparatus for drying finely-divided material
1,151,553	Aug. 31, 1915	Adler, Rudolf	Process of making animal charcoal
1,158,965	Nov. 2, 1915	Beatty, W. A.	Process of depositing carbon in porous substances
1,160,657	Nov. 16, 1915	Ritchay, V. O., Trimmer, H. A.	Bone-burner
1,177,725	Apr. 4, 1916	Scott, J. W.	Process of reconditioning bone-black
1,184,397	May 23, 1916	Weinrich, M.	Process of revivifying or decarbonizing bone-black and other filtering media
1,184,398	do	do	Apparatus for revivifying and for decarbonizing bone-black and other media
1,195,720	Aug. 22, 1916	Pilaski, L.	Process of making active charcoal powder
1,207,178	Dec. 5, 1916	Kent, R. S.	Apparatus for revivifying char
1,262,769	Apr. 16, 1918	Garner, J. B., Clayton, H. D.	Manufacture of chlorinated hydrocarbons
1,269,080	June 11, 1918	Hayashi, Takakazu, Emura, Umejiro	Process of treating phosphoric acid to be used as a clarifier
1,308,826	July 8, 1919	Weinrich, M.	Method of manufacturing carbonaceous filtering mediums
1,356,631	Oct. 26, 1920	Kennedy, C. F.	Revivification of filtering agents
1,399,503	Dec. 6, 1921	McCrae, G.	Cylindrical kiln and drier
1,430,200	Sept. 26, 1922	Tiemann, F.	Process for purifying sugar juices by filtration and decantation
1,434,023	Oct. 31, 1922	Peiter, F.	Rotary kiln
1,440,095	Dec. 26, 1922	Mosher, C. D.	Fuel-burning apparatus
1,440,194	do	Wijnberg, A.	Method of drying, burning, and recovering finely divided material
1,443,529	Jan. 30, 1923	Dworzak, A.	Rotary furnace or kiln
1,446,857	Feb. 27, 1923	Peiter, F.	Kiln
1,447,461	Mar. 6, 1923	Brewster, J. F., Raines, W. G., Jr.	Method for employing decolorizing carbons and other adsorbing materials
1,448,846	Mar. 20, 1923	Jordan, W. L.	Process for making a composition for purifying liquids

TABLE 30—*Continued*

Patent No.	Date	Patentee	Title
1,473,491	Nov. 6, 1923	Manning, F. W.	Method and apparatus for treating materials for filtering, decolorizing, and similar purposes
1,475,502	Nov. 27, 1923	do	Method of revivifying finely-divided Fuller's earth, bone char, and the like
1,490,846	Apr. 15, 1924	Norbek, J.	Furnace
1,496,229	June 3, 1924	Jones, W.	Filtering Medium
1,500,862	July 8, 1924	Bonaparte, S. G.	Drier
1,507,521	Sept. 2, 1924	Russell, M.	Process for revivifying filters
1,513,622	Oct. 28, 1924	Manning, F. W.	Apparatus for revivifying purifying materials
1,533,866	Apr. 14, 1925	Kent, E. C.	Rotary Kiln
1,551,075	Aug. 25, 1925	Thienemann, H.	Highly-active charcoal
1,559,054	Oct. 27, 1925	Smith, A. W.	Method of manufacture of prepared charcoal
1,592,599	July 13, 1926	Davis, C. B.	Synthetic bone char and method of producing same
1,602,678	Oct. 12, 1926	Kent, R. S.	Sectional retort for retort kilns
1,624,296	Apr. 12, 1927	Welle, H. C.	Method of treating sugar
1,692,745	Nov. 20, 1928	Kemp, W. W.	Method of treating bone-black or char
1,755,156	Apr. 15, 1930	Urbain, E.	Bone-black of great decolorizing power
1,758,202	May 13, 1930	Rice, E. W.	Method of and apparatus for reactivating charcoal
1,784,626	Dec. 9, 1930	Hamill, J.	Bone-char-drying apparatus
1,829,741	Nov. 3, 1931	DeVries,	Drier
1,856,302	May 3, 1932	Wheeler, T. L., Carpenter, J. B.	Method of making bone-black
1,863,803	June 21, 1932	Pantenburg, V.	Apparatus for the regeneration of adsorption material
1,891,407	Dec. 20, 1932	Godel, A.	Activation of carbonaceous substances
1,917,339	July 11, 1933	Straitz, J. F.	Char retort
1,918,367	July 18, 1933	Ackermann, A.	Apparatus for activation of carbonaceous substances
1,934,930	Nov. 14, 1933	Kent, R. S.	Drier and granulator
1,962,643	June 12, 1934	do	Drier
1,966,553	July 17, 1934	Kropp, C. L.	Absorbent briquette
1,971,895	Aug. 28, 1934	Andrews, N. R.	Process of reclaiming bone-black and like materials
2,000,972	May 14, 1935	Manross, B.	Revivifier
2,046,687	July 7, 1936	Kent, R. S.	Kiln retort structure

TABLE 30—*Concluded*

Patent No.	Date	Patentee	Title
2,064,813	Dec. 22, 1926	Andrews, N. R.	Apparatus for utilizing furnace gases in the reclaiming of bone-black and like materials
2,073,388	Mar. 9, 1937	Elliott, R. D., Elliott, M. J.	Means for treating liquids
2,076,647	Apr. 13, 1937	Johnson, B. M.	Apparatus for revivifying charcoal
2,082,656	June 1, 1937	Reichert, J. S., Elliott, R. B.	Process of purification of sugar solutions
2,083,756	June 15, 1937	Vissac, G. A.	Apparatus for drying and treating wet granular materials
2,170,601	Aug. 22, 1939	Wilson, S. M., Waggaman, W. H.	Process of producing material for purifying liquids
2,178,587	Nov. 7, 1939	Kauffmann, H. O.	Decolorizing sugar solutions
2,209,069	July 23, 1940	Bodenheim, F. A., Heath, C. E.	Adsorbent material and process
2,226,421	Dec. 24, 1940	Barrett, E. P., Beal, G. D.	Bone-black
2,277,854	Mar. 31, 1942	Lecoq, L. P. V.	Colloidal tertiary calcium phosphate
2,352,932	July 4, 1944	Barrett, E. P., West, J. R.	Adsorbent
2,369,139	Feb. 13, 1945	Deitz, V. R.	Method of treating bone-black
2,372,996	Apr. 3, 1945	Wickenden, L.	Method of treating sugar melts
2,391,116	Dec. 18, 1945	Ashley, K. D.	Method of producing granular adsorbent

TABLE 31. U. S. PATENTS ON PHOSPHATES IN GLASS AND CERAMIC PRODUCTS

Patent No.	Date	Patentee
295,410	Mar. 18, 1884	Knaffl, L.
1,570,202	Jan. 19, 1926	Buck, E. C.
1,961,603	June 5, 1934	Berger, E.
1,964,629	June 26, 1934	Crimm, H. G. and Huppert, P.
2,031,958	Feb. 25, 1936	Kaufmann, W. and Bungartz, E.
2,042,425	May 26, 1936	Kaufmann, W. *et al.*
2,100,391	Nov. 30, 1937	Grimm, H. G. and Huppert, P.
2,194,784	Mar. 26, 1940	Berger, E.
2,226,418	Dec. 24, 1940	Tillyer, E. D. *et al.*
2,227,082	Dec. 31, 1940	Grimm, H. G. and Huppert, P.
2,232,462	Feb. 18, 1941	Lower, D. E.
2,252,588	Aug. 12, 1941	Whitesell, R. J.
2,266,646	Dec. 16, 1941	Lower, D. E.
2,278,501	Apr. 7, 1942	Tillyer, E. D. *et al.*
2,359,789	Oct. 10, 1944	Pincus, A. G.
2,381,925	Aug. 14, 1945	do
2,393,469	Jan. 22, 1946	Hooley, Jr. G.
2,415,661	Feb. 11, 1947	Sun, K. H. and Huggins, M. L.
2,423,128	July 1, 1947	Tillyer, E. D.
2,427,728	Sept. 23, 1947	Jenkins, H. G. *et al.*
2,430,539	Nov. 11, 1947	Sun, K. H.
2,441,853	May 18, 1948	Stanworth, J. E.
2,455,413	Dec. 7, 1948	Froelich, H. C. *et al.*
2,455,414	do	do
2,455,415	do	Froelich, H. C.
2,496,824	Feb. 7, 1950	Sun, K. *et al.*
2,518,194	Aug. 8, 1950	Silverman, A. *et al.*

TABLE 32. U. S. PATENTS ON PHOSPHATE FLAMEPROOFING PRODUCTS

Patent No.	Date	Patentee
724,788	Apr. 7, 1903	Blenio, G.
802,311	Oct. 17, 1905	Patten, W. D.
1,030,909	July 2, 1912	Mesturina, G. A.
1,080,966	Dec. 9, 1913	Hall, W. A.
1,116,349	Nov. 3, 1914	Zeller, W. C.
1,133,385	Mar. 30, 1915	Lindsay, W. G.
1,271,506	July 2, 1918	Ferguson, G. E.
1,274,171	July 23, 1918	Majot, E.
1,310,841	July 22, 1919	Robinson, E. G.
1,329,386	Feb. 3, 1920	Emhardt, J. C.
1,382,618	June 28, 1921	Blenio, G.
1,397,028	Nov. 15, 1921	Wortelmann, G. A.
1,436,231	Nov. 21, 1922	Blenio, G.
1,501,895	July 22, 1924	Andrews, L. W. and Mathias, L. D.
1,501,911	do	Mathias, L. D.
1,523,813	Jan. 20, 1925	Lindsay, W. G.
1,523,814	do	do
1,594,201	July 27, 1926	Horan, C.
1,743,176	Jan. 14, 1930	Winckler, W. J.
1,804,633	May 12, 1931	McKee, R. H.
1,837,150	Dec. 15, 1931	Dreyfus, C. *et al.*
1,870,972	Aug. 9, 1932	Theumann, M. J.
1,886,775	Nov. 8, 1932	Zelger, G. E.
1,917,176	July 4, 1933	Winogradow, A.
1,938,746	Dec. 12, 1933	Engelhardt, R.
1,945,714	Feb. 6, 1934	Winogradow, A.
1,975,072	Oct. 2, 1934	Booth, C. F.
1,985,771	Dec. 25, 1934	Eichengrün, A.
2,030,653	Feb. 11, 1936	Quinn, R. G.
2,032,605	Mar. 3, 1936	Whitehead, W.
2,036,854	Apr. 7, 1936	Dickie, W. A. and Hill, F. B.
2,071,353	Feb. 23, 1936	Morgan, W. L.
2,071,354	do	do
2,089,697	Aug. 10, 1937	Groebe, F.
2,097,509	Nov. 2, 1937	Boller, E. R.
2,167,278	July 25, 1939	Leathermann, M.
2,194,827	Mar. 26, 1940	Gordon, A.
2,212,152	Aug. 20, 1940	Cupery, M. E.
2,225,831	Dec. 24, 1940	Herz, W.
2,233,475	Mar. 4, 1941	Dreyfus, H.
2,262,634	Nov. 11, 1941	Cobbs, W. W.
2,286,308	June 16, 1942	Rosser, C. M.
2,286,726	do	Gordon, W. E.
2,302,107	Nov. 17, 1942	Datlow, J.
2,305,035	Dec. 15, 1942	Rosser, C. M.
2,343,186	Feb. 29, 1944	Hopkinson, H.
2,368,660	Feb. 6, 1945	Hockstetter, F. W.

TABLE 32—*Concluded*

Patent No.	Date	Patentee
2,378,714	July 19, 1945	Leathermann, M.
2,386,471	Oct. 9, 1945	Jones, G. *et al.*
2,401,440	June 4, 1946	Thomas, C. A. *et al.*
2,407,668	Sept. 17, 1946	Leatherman, M.
2,418,525	Apr. 8, 1947	Pollak, F. F.
2,418,843	Apr. 15, 1947	Leatherman, M.
2,421,218	May 27, 1947	Pollak, F. F.
2,461,302	Feb. 8, 1949	Truhlar, J.
2,464,342	Mar. 15, 1949	Pollak, F. F. *et al.*
2,470,042	May 10, 1949	McLean, A. *et al.*
2,471,042	do	do
2,472,335	June 7, 1949	do
2,475,626	July 12, 1949	Leathermann, L.
2,482,755	Sept. 27, 1949	Ford, F. M. and Hall, W. P.
2,482,756	do	do
2,523,626	Sept. 26, 1950	Jones, G. Jr. *et al.*
2,526,083	Oct. 17, 1950	Nielson, M. L.
2,526,427	do	Simon, E. *et al.*
2,526,462	do	Edelstein, O.

TABLE 33. U. S. PATENTS ON MISCELLANEOUS PHOSPHATE PROCESSES AND PRODUCTS

Patent No.	Date	Patentee
54,635	May 8, 1866	Wister, J.
171,857	Jan. 4, 1876	Ravenel, St. J.
209,980	Nov. 19, 1878	Pirz, A.
238,133	Feb. 22, 1881	Lewis, Geo. T.
423,320	Mar. 11, 1890	Hudgkins, E. R.
517,661	Apr. 3, 1894	Powter, N. B.
517,662	do	do
792,314	June 13, 1905	Chisolm, W. B.
824,280	June 26, 1906	do
824,281	do	do
947,795	Feb. 1, 1910	Coates, L. R.
947,796	do	do
1,002,248	Sept. 5, 1911	Ellis, C.
1,024,880	Apr. 30, 1912	Coates, L. R.
1,104,326	July 20, 1914	Stoltzenberg, H.
1,147,926	July 27, 1915	Chisolm, W. B.
1,222,112	Apr. 10, 1917	Lipman, J. G.
1,235,906	Aug. 7, 1917	do
1,261,025	Apr. 2, 1918	Hoff, J. N.
1,316,396	Sept. 16, 1919	Snelling, W. O.
1,348,990	Aug. 10, 1920	Giesecke, A.
1,361,596	Dec. 7, 1920	Lipman, J. G.
1,425,747	Aug. 15, 1922	Coates, L. R.
1,440,836	Jan. 2, 1923	Morgan, E. A.
1,445,167	Feb. 13, 1923	Plauson, H.
1,472,675	Oct. 30, 1923	Reed, M. C.
1,501,915	July 22, 1924	Nikaido, Y.
1,607,666	Nov. 23, 1926	De Haen, W.
1,617,098	•Feb. 8, 1927	Blumenberg, H., Jr.
1,633,959	June 28, 1927	Smolezyk, E.
1,678,775	July 31, 1928	Gravell, J. H.
1,713,868	May 21, 1929	Edwards, R. S.
1,777,908	Oct. 7, 1930	Bodero, B.
1,783,417	Dec. 2, 1930	Durgin, C. B. *et al.*
1,859,250	May 17, 1932	Bertel, R.
1,884,558	Oct. 25, 1932	Calcott, W. *et al.*
2,020,649	Nov. 12, 1935	Ipatieff, V.
2,037,316	Oct. 13, 1936	Rutherford, C. H.
2,078,627	Apr. 27, 1937	Block, L. *et al.*
2,087,230	July 20, 1937	Bigeon, J. A. M.
2,091,178	Aug. 24, 1937	Gilbert, H. N. *et al.*
2,092,913	Sept. 14, 1937	Fiske, A. H.
2,095,366	Oct. 12, 1937	Marsico, S. E.
2,095,993	Oct. 19, 1937	MacIntire, W. H.
2,096,742	Oct. 26, 1937	Hale, W. J.
2,097,446	Nov. 2, 1937	Claiborne, J. L. and Peterson, P. D.
2,102,119	Dec. 14, 1937	Henkel, L. C.

TABLE 33—*Continued*

Patent No.	Date	Patentee
2,108,940	Feb. 22, 1938	MacIntire, W. H.
2,111,532	Mar. 15, 1938	Hagood, Johnson
2,120,212	June 7, 1938	Curtin, L. P.
2,120,702	June 14, 1938	Ipatieff, V. *et al.*
2,121,520	June 21, 1938	Curtin, L. P.
2,126,793	Aug. 16, 1938	MacIntire, W. H. *et al.*
2,130,557	Sept. 20, 1938	Munter, C. J.
2,132,000	Oct. 4, 1938	Curtin, L. P.
2,132,439	Oct. 11, 1938	Romig, G. C.
2,133,286	Oct. 18, 1938	Fiske, A. H.
2,133,289	do	Fraser, L. H. D.
2,133,290	do	do
2,133,310	do	do
2,133,311	do	Shuman, R. L.
2,134,706	Nov. 1, 1938	do
2,137,674	Nov. 22, 1938	Dirby, I. H. and Cunningham, O. D.
2,137,792	do	MacIntire, W. H.
2,138,029	Nov. 29, 1938	Woodstock, W. H.
2,138,870	Dec. 6, 1938	Fiske, A. H.
2,142,870	Jan. 3, 1939	Lowes, D. E.
2,142,871	do	Hall, L. A. and Griffith, C. L.
2,148,378	Feb. 21, 1939	do
2,148,634	Feb. 28, 1939	Malishev, Boris
2,151,984	Mar. 28, 1939	do
2,157,164	May 9, 1939	Moyle, C. L. and Bass, S. L.
2,158,154	May 16, 1939	Daly, A. J. and Lowe, W. G.
2,159,381	May 23, 1939	Rose, J. R.
2,160,232	May 30, 1939	Jochum, Kurt, Glier, Herman and Pauser, Karl
2,160,233	do	Schiaeger, J. R.
2,160,700	do	do
2,160,701	do	Knox, W. H.
2,161,035	June 6, 1939	do
2,162,655	June 13, 1939	Gilbert, H. W.
2,163,065	June 20, 1939	Volkel, W.
2,163,901	June 27, 1939	Rosenstein, L.
2,164,228	do	Walker, W. C.
2,168,169	Aug. 1, 1939	Burns, J. R.
2,169,576	Aug. 15, 1939	Meyer, O.
2,170,274	Aug. 22, 1939	Booth, C. F.
2,170,601	do	Morgan, W. L.
2,173,103	Sept. 19, 1939	Wilson, S. M. *et al.*
2,173,376	do	Fraser, L. H.
2,194,827	Mar. 26, 1940	Rose, J. R.
2,200,742	May 14, 1940	Gordon, A.
2,200,743	do	Hardy, C.
2,204,157	June 11, 1940	do
2,206,226	July 2, 1940	Semon, W. L.
		Groombridge, W. H. *et al.*

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Patent No.	Date	Patentee
2,213,127	Aug. 27, 1940	Kerschbaum, F. P. *et al.*
2,216,552	Oct. 1, 1940	Gage, W. P.
2,222,734	Nov. 26, 1940	Bancroft, W. D. *et al.*
2,222,735	do	do
2,222,736	do	do
2,222,737	do	do
2,222,738	do	do
2,227,082	Dec. 31, 1940	Grimm, H. *et al.*
2,227,432	Jan. 7, 1941	Behrman, A. S.
2,227,928	do	Drucker, Julius
2,232,462	Feb. 18, 1941	Lower, D. E.
2,252,588	Aug. 12, 1941	Whitesell, R. J.
2,257,281	Sept. 30, 1941	Scholz, H. A.
2,260,819	Oct. 21, 1941	Ballasa, L.
2,261,174	Nov. 4, 1941	McCauley, R. B.
2,262,634	Nov. 11, 1941	Cobbs, W. W.
2,266,646	Dec. 16, 1941	Lower, D. E.
2,271,374	Jan. 27, 1942	MacKay, C. J.
2,291,958	Aug. 4, 1942	Garrison, A. D.
2,301,913	Nov. 17, 1942	Veltman, P. L.
2,324,079	July 13, 1943	Greger, H. H.
2,330,865	Oct. 5, 1943	Butzler, E. W.
2,336,651	Dec. 14, 1943	Stratford, R. K.
2,336,793	do	Layng, E. T., *et al.*
2,341,581	Feb. 15, 1944	Teichmann, C. F.
2,352,168	June 27, 1944	Christensen, L. M.
2,355,081	Aug. 8, 1944	Julian, P. L., *et al.*
2,363,011	Nov. 21, 1944	Michalek, J. C.
2,364,970	Dec. 12, 1944	Gwynn, M. H.
2,367,877	Jan. 23, 1945	Layng, E. T.
2,369,301	Feb. 13, 1945	Kerschbaum, F. P.
2,369,693	Feb. 20, 1945	Tollefson, R. C.
2,375,638	May 8, 1945	England, L. H.
2,384,502	Sept. 11, 1945	Streicher, J. S.
2,385,832	Oct. 2, 1945	Musselman, J. M.
2,391,493	Dec. 25, 1945	Wainer, Eugene and Salomon, Allen
2,395,126	Feb. 19, 1946	King, C. S.
2,396,859	Mar. 19, 1946	Latchum, J. W.
2,396,918	do	Hubbard, F. E. and McCullough, C. R.
2,408,784	Oct. 8, 1946	Lange, W. *et al.*
2,408,785	do	Lange, W.
2,414,974	Jan. 28, 1946	Nielson, M. L.
2,415,661	Feb. 11, 1947	Sun, Kuan-Han *et al.*
2,416,807	Mar. 4, 1947	Watkins, F. M.
2,417,462	Mar. 18, 1947	Adler, H.
2,417,804	Mar. 25, 1947	do
2,418,422	Apr. 1, 1947	Palmer, R. C.

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Patent No.	Date	Patentee
2,418,843	Apr. 15, 1947	Leatherman, M.
2,420,859	May 20, 1947	Buckner, O. S.
2,423,128	July 1, 1947	Tilyer, E. D.
2,423,154	do	O'Brien, J. W.
2,423,895	July 15, 1947	Lange, W. *et al.*
2,424,992	Aug. 5, 1947	Lee, R.
2,426,394	Aug. 26, 1947	Hall, R. E. *et al.*
2,426,678	Sept. 2, 1947	Greenberg, H.
2,427,728	Sept. 23, 1947	Jenkins, H. C. *et al.*
2,427,847	do	Fryling, C. F.
2,430,400	Nov. 4, 1947	Hoelscher, A. P.
2,430,539	Nov. 11, 1947	Sun, Kuan-Han
2,432,095	Dec. 9, 1947	Frey, D. R.
2,440,303	Apr. 26, 1948	Silverstein, M. S.
2,441,853	May 18, 1948	Stanworth, J. E.
2,450,952	Oct. 5, 1948	Greger, H. H.
2,451,748	Oct. 19, 1948	Kraybill, H. R. *et al.*
2,454,056	Nov. 16, 1948	Greger, H. H.
2,455,413	Dec. 7, 1948	Froelich, H. C. *et al.*
2,455,414	do	do
2,455,758	do	Greger, H. H.
2,456,367	Dec. 14, 1948	Britton, E. C. *et al.*
2,456,368	do	do
2,458,292	Jan. 4, 1949	Munter, C. J.
2,459,090	do	Otto, F. P. and Meyer, R. O.
2,459,113	do	Oberright, E. A.
2,459,115	do	do
2,463,429	Mar. 1, 1949	Roberts, E. N.
2,463,792	Mar. 8, 1949	Morgan, W. L.
2,464,902	Mar. 22, 1949	Stuart, K. B.
2,465,292	do	Sparks, W. J. *et al.*
2,470,136	May 17, 1949	Bramberry, H. M.
2,471,115	May 24, 1949	Mikeska, L. A.
2,472,379	June 7, 1949	Lawson, H. E.
2,472,616	do	Prescott, W. G. *et al.*
2,476,654	July 19, 1949	Froelich, H. C.
2,476,676	do	McKeag, A. H.
2,481,807	Sept. 13, 1949	Anderson, C. C.
2,481,700	do	Sun, K. H. and Higgins, M. L.
2,481,807	do	Anderson, D. E.
2,482,104	Sept. 20, 1949	Dolian, F. E.
2,482,750	Sept. 27, 1949	Erickson, A. M. *et al.*
2,488,298	Nov. 15, 1949	Lange, W. *et al.*
2,488,299	do	do
2,521,514	Sept. 5, 1950	Hartough, H. D.
2,521,676	Sept. 12, 1950	Schmidt-Nickels, W.
2,522,548	Sept. 19, 1950	Streicher, J. S.
2,525,144	Oct. 10, 1950	Mavity, J. M.
2,525,145	do	do

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